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STATISTICAL OXIDANT/PRECURSOR RELATIONSHIPS FOR THE LOS ANGELES REGION

Interim Report

Part 1. Data Quality Review and Evaluation

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by

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ABSTRACT

This interim document reports on Phase I studies for a project involving "Statistical Oxidant/Precursor Relationships in the Los Angeles Basin." The purpose of Phase I is to survey the availability of aerometric data in the SCAB and SEDAB, to identify potential source and receptor sites, and to assess the quality of the data base. The objective is to investigate whether or not the existing data base is sufficiently comprehensive and accurate for empirical modeling of the oxidant/precursor relationship.

A survey of data availability indicates that there is an abundance of oxidant and precursor data for conducting the empirical modeling study. There is also an adequate amount of meteorological data. All of the air quality data and much of the meteorological data are readily available in computerized form.

A review of wind streamline and trajectory studies demonstrates that a westerly sea breeze flow occurs almost invariably during daylight hours in the June-October photochemical smog season. For this prevailing wind pattern, it is possible to identify at least five groups of source/receptor sites for the empirical modeling analysis.

A review of monitoring methods and statistical tests of data quality result in consistent conclusions concerning the precision of oxidant and precursor measurements. The precision of the data can be summarized as OX/O_3 - excellent, NO_x - good, THC - fair, and NMHC - poor. Poor data quality precludes the use of NMHC data in empirical modeling studies. Statistical oxidant/precursor relationships for the Los Angeles Region should be based on data for OX/O_3, NO_x, and THC.

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1.0 INTRODUCTION

The South Coast Air Basin* (SCAB) experiences a severe problem with respect to photochemical oxidant pollution. During the summer and early fall, the National Ambient Air Quality Standard (.08 ppm, 1 hour average) is exceeded almost every day, typically by a factor of two to four. On days of extreme photochemical smog in the SCAB, oxidant values up to five or six times the national standard are reached.

The formulation and evaluation of oxidant control strategies for the SCAB have been hindered by the lack of a reliable methodology for relating ambient oxidant levels to precursor (hydrocarbon and nitrogen oxide) emission levels. There is a pressing need for oxidant air quality models that are complex enough to include the realities of the problem but simple enough to be useful in practice. Under contract to the California Air Resources Board, Technology Service Corporation is developing empirical models of the relationship of oxidant to its precursors by performing a statistical analysis of the existing SCAB aerometric data base.

The empirical modeling project is divided into four phases:

I. Data quality review and evaluation

II. Data acquisition and creation of a data base

III. Model development and verification

IV. Application of the model to determining the impact of auto use reductions on oxidant levels.

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*Federal designation: Metropolitan Los Angeles Air Quality Control Region.

This interim report presents the results of Phase I. This phase is critical because questions have been raised concerning the quality of the aerometric data base for the purpose of empirical modeling. The ARB and EPA Project Officers will decide if the results of Phase I warrant continuation to subsequent parts of the study.

1.1 ORGANIZATION OF PHASE I

The purpose of Phase I is to survey the existing aerometric data base, to conduct data quality tests, and to verify that the data base is sufficiently accurate and comprehensive for the empirical modeling study. Phase I consists of five major tasks:

A. Documentation of Data Sources

- Identification of monitoring locations for oxidant, NO_x, hydrocarbons, and weather parameters
- Documentation of data sources, quantity of data, monitoring methods, and data availability

B. Selection of Potential Precursor/Receptor Sites

- Review of studies concerning wind trajectories and wind streamlines
- Identification of precursor/receptor situations for the dominant daytime wind flow patterns of the photochemical smog season

C. Review of Monitoring Methods

- Review of literature concerning air pollution monitoring methods, including studies of chemical interferences,

measurement reproducibility, and other problems associated with the various methods

- Assessment of the specific practices followed by the monitoring agencies in the SCAB

D. Data Verification Against Special Monitoring Practices

- Check of routine monitoring data against parallel measurements taken in the ARB Mobile Van Program
- Check of routine hydrocarbon data against field tests conducted by the ARB El Monte Laboratory

E. Interstation Correlations

- Estimation of the correlation of pollutant levels between various monitoring stations in the basin
- Comparison of interstation correlations for different pollutants

Chapters 2 through 6 discuss the five tasks in the order listed above. Chapter 7 describes the findings and conclusions that are reached. A summary of the conclusions is given in Section 1.2, while TSC's recommendations are presented in Section 1.3.

1.2 SUMMARY OF CONCLUSIONS

Chapter 7 of this report discusses the findings and conclusions that have resulted from the Phase I studies. An overview of the conclusions is presented in the paragraphs which follow:

- An abundance of air quality data exists in the SCAB and SEDAB for conducting the empirical modeling analysis. There is also an adequate amount of meteorological data. All of the air quality data and much of the meteorological data are available in computerized form.

- A westerly sea breeze flow occurs almost invariably during daytime hours in the June-October photochemical smog season. For this dominant wind pattern, it is possible to identify at least five groups of source/receptor monitoring sites representing various transport distances and various reaction times.
- A critical review of monitoring methods and statistical tests of data quality lead to consistent conclusions concerning the quality of oxidant and precursor measurements. The precision of the data can be summarized as follows:

OX/O_3	Excellent
NO_x	Good
THC	Fair
NMHC	Poor

- The absolute accuracy of KI oxidant data can be improved by correcting for SO_2 and NO_2 interference and by adjusting for calibration differences.
- Routine NMHC data exhibit poor quality because the methane separation methods are error-prone, because errors are compounded by subtracting one uncertain measurement from another, and because the data are reported with a large round-off error.
- It should be feasible to conduct a meaningful empirical modeling study with data for oxidant/ozone, NO_x and THC. The results of previous empirical modeling efforts with Los Angeles data provide some encouragement in this regard.

1.3 RECOMMENDATIONS

The Phase I studies warrant the following recommendations:

- Empirical modeling of the oxidant/precursor relationship should not be attempted using routine NMHC data. If the present project is continued to subsequent phases, the empirical analysis should be based on data for oxidant/ozone, NO_x, and THC. The main drawbacks to such an analysis would be the "fair" quality of THC data and the approximations made in estimating NMHC concentrations from THC measurements.
- In a project continuation, a preliminary statistical analysis should be conducted involving daily wind data and correlations between precursor measurements and oxidant measurements. This preliminary analysis should allow a more exact assessment of transport relationships between source sites and receptor sites; it also should help to identify precursor sites with the highest quality THC data.
- If conducted, the empirical modeling study should be restricted to days exhibiting the westerly sea breeze flow pattern. Selection of specific source/receptor sites and oxidant averaging times each day should be based on analyses of daily wind speeds and wind directions.

2.0 DOCUMENTATION OF DATA SOURCES

This chapter documents the availability of air quality and meteorological data for empirical modeling of the oxidant/precursor relationship. The discussion covers quantities of data, years for which data are available, monitoring methods, data sources, and monitor locations. The area of interest includes the South Coast Air Basin (SCAB) and adjacent parts of the Southeast Desert Air Basin (SEDAB).

2.1 AIR QUALITY DATA

The empirical modeling analysis requires hourly data for hydrocarbons and nitrogen oxides at source sites in the SCAB and hourly data for oxidant (or ozone) at receptor sites in the SCAB and SEDAB. To conduct the analysis, at least three years of simultaneous oxidant and precursor data are necessary. This section lists those monitoring sites which provide sufficient air quality data and documents monitoring methods, site locations, and data availability. Much of the information presented below is based on state and local data summaries.[1,2,3]

2.1.1 Ambient Precursor Data

In order to select potential precursor sites for the empirical modeling analysis, all sites in the SCAB which monitor both total hydrocarbons (HC) and nitrogen oxides (NO_x) were identified. The number of hourly HC and NO_x readings at each site was documented for each year from 1966 to 1975. Table 2.1 lists the sites which provide "complete" data for at least three years. The completeness criterion requires that at least 6500 hourly readings

Table 2.1 Number of Hourly HC and NO_x Readings at SCAB Sites by Year (Hundreds of Measurements).[+]

Site (Station Number)	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975
LOS ANGELES COUNTY[*]										
Azusa (60)	--	23	83	84	85	82	86	87	87	86
	77	77	76	78	72	79	79	80	82	80
Burbank (69)	--	--	--	--	41	85	86	86	85	87
	77	76	76	77	77	78	85	85	82	82
Lennox (76)	--	--	--	--	53	86	87	85	87	86
	74	75	73	77	80	80	83	83	81	82
Los Angeles (1)	84	80	85	83	83	86	87	87	85	82
	78	74	76	70	77	79	79	75	79	79
Newhall (81)	--	--	--	--	58	84	86	84	86	87
	--	--	--	--	25	79	80	82	82	82
Pasadena (79)	--	--	22	81	80	82	34			
	--	--	31	79	79	80	33			
Pasadena (83)							52	86	85	86
							51	84	81	82
Pomona (75)	--	--	--	--	50	86	87	87	87	87
	76	75	78	79	79	81	82	84	82	83
Reseda (74)	--	--	--	--	46	85	85	86	85	85
	77	76	76	77	77	78	83	85	84	84
Whittier (80)	--	--	--	--	61	85	85	86	80	85
	--	--	--	29	78	80	83	81	81	83
ORANGE COUNTY										
Anaheim (377)	78	76	84	82	83	78	87	86	77	80
	54	73	74	79	73	78	79	72	81	76
SAN BERNARDINO COUNTY										
San Bernardino (351)	81	82	86	81	79	86	82	85	86	86
	43	59	54	32	26	21	68	74	80	79

[+]Upper entry is number of total hydrocarbon readings; lower is number of NO_x readings.

[*]NMHC and CH_4 data, as well as total hydrocarbon data, are available for Los Angeles County sites.

(75% of the total hours in a year) exist for HC and for NO_x. The upper entry of each pair in Table 2.1 is the number of recorded hydrocarbon readings for a given site and year, while the lower figure is the corresponding number of NO_x readings. The smaller of these two numbers is the maximum number of hours for which both HC and NO_x readings might be available for a given site and year. The actual number of hours with simultaneous HC and NO_x data may be somewhat smaller, depending on the correlation between missing HC values and missing NO_x data. Station-years not meeting the completeness criterion for both pollutants are shaded in the table.

All sites in Los Angeles County which monitor HC also monitor methane (CH_4) and report nonmethane hydrocarbons (NMHC = HC - CH_4) as well as total hydrocarbons.[4] Since methane has negligible photochemical reactivity, it seems preferable to use NMHC instead of total hydrocarbons in the empirical modeling analysis. However, the lack of NMHC data at all sites outside Los Angeles County will necessitate the use of total hydrocarbon data in some portions of the analysis. As long as a fairly consistent relationship exists between HC and NMHC at each site, the error induced by using HC measurements rather than NMHC measurements should not be significant.*

*As will be discussed later, total hydrocarbon measurements in Los Angeles County appear to be much more reliable than NMHC measurements. This is partly due to the large round-off error in the NMHC readings. If statistical analyses demonstrate that the quality of NMHC data is poor, then NMHC data will be entirely excluded from this study.

It should be noted that hydrocarbon monitoring has recently begun at a number of sites. These sites may be useful for future studies, but they have not accumulated enough data to be considered for the present project.

2.1.2 Ambient Oxidant (Ozone) Data

A large number of sites in the SCAB and SEDAB monitor oxidant or ozone. Ozone is a specific chemical species, O_3, which is measured by the chemiluminescent method or by ultraviolet photometry. Oxidant consists mostly of ozone but includes other oxidizing pollutants in the atmosphere. As defined here, oxidant data refer to measurements taken by the colorimetric potassium iodide (KI) method. For the monitoring sites discussed below, all pre-1973 data (and most of the data thereafter) consist of oxidant measurements rather than ozone measurements.

Table 2.2 lists the monitoring sites in the SCAB that provide at least three years of "complete" oxidant or ozone data, while Table 2.3 presents a similar listing for the SEDAB. The numbers given in Tables 2.2 and 2.3 refer to the number of hourly readings taken each year. The completeness criterion requires that at least 6500 hourly readings be available for each station-year included in the study. As before, station-years not meeting the completeness criterion are shaded.

As explained in Chapter 4, oxidant measurements made using the KI method can be converted to equivalent ozone concentrations by corecting for interferences by sulfur dioxide and nitrogen dioxide. Thus, it is also necessary

Table 2.2 Number of Hourly Oxidant Readings at SCAB Sites by Year (Hundreds of Measurements)

Site (Station Number)	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975
LOS ANGELES COUNTY										
Azusa (60)	83	80	82	82	83	83	82	82	83	83
Burbank (69)	83	80	82	82	83	82	82	83	83	82
Lennox (76)	83	82	82	81	81	81	83	83	83	83
Long Beach (72)	82	82	81	79	80	83	82	82	81	81
Los Angeles (1)	83	82	82	82	79	82	84	84	80	82
Newhall (81)	--	--	--	19	79	79	82	83	82	82
Pasadena (89) (83)	--	--	33	82	80	83	33 51	83	82	81
Pomona (75)	82	83	83	82	83	82	83	83	83	81
Reseda (74)	82	83	81	82	81	82	84	84	83	83
West LA (71)	81	83	82	82	83	81	83	82	82	83
Whittier (80)	--	--	--	30	83	83	82	83	83	83
ORANGE COUNTY										
Anaheim (377)	77	77	81	77	73	77	80	82	81	42
La Habra (378)	--	14	79	58	77	77	80	81	79	76*
SAN BERNARDINO COUNTY										
Redlands (365)	--	12	78	67	77	75	75	85*	86*	86*
San Bernardino (351)	80	83	82	79	78	79	79	77*	87*	83*
RIVERSIDE COUNTY										
Riverside (326)	74	74	33	--	--	80	54			
Rubidoux (344)							29	86	84	84

*All or part of the oxidant data for these station-years are ozone data.

Table 2.3 Number of Hourly Oxidant Readings at SEDAB Sites by Year (Hundreds of Measurements).

Site (Station Number)	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975
LOS ANGELES COUNTY										
Lancaster (82)	--	--	--	--	14	78	83	80	81	82
RIVERSIDE COUNTY										
Banning (333) (350)	--	--	--	--	--	58	82	84	83	84
Indio-Oasis (345)	--	--	--	--	--	66	80	85	85	85
Palm Springs (331)	--	--	--	--	--	63	82	85	85	81
SAN BERNARDINO COUNTY										
Victorville (369)	--	--	44	73	34	74	79	77	82	81

to assess the availability of SO_2 and NO_2 data. Tables 2.4 and 2.5 summarize the availability of SO_2 and NO_2 data for the sites which provide "complete" oxidant data (i.e., the sites in Tables 2.2 and 2.3). It is obvious that the lack of SO_2 data for some years at some sites may present a problem. However, most sites which lack SO_2 data experience low SO_2 levels, and therefore should have low SO_2 interference. A decision on how to make inteference corrections for sites (or years) lacking SO_2 or NO_2 data will be left for Phase II of this program.*

2.1.3 Monitoring Methods

Table 2.6 lists the monitoring methods for hydrocarbons, NO_x, and oxidant/ozone in the SCAB and for oxidant/ozone in the SEDAB. As discussed in Chapter 4, different monitoring methods will not necessarily yield equivalent measurements. Fortunately, the various air pollution agencies in the SCAB use similar methods for hydrocarbons and NO_x. However, four different techniques are used for oxidant or ozone. In order to develop a data base that is internally consistent, it will be necessary to apply correction factors to compensate for differences among the measurement techniques for oxidant or ozone. The appropriate correction factors are presented in Chapter 4.

2.1.4 Data Availability

For the sites listed in Tables 2.1 to 2.6, the monitoring agencies are the respective county branches of the Southern California Air Pollution Control Districy (SCAPCD). The California Air Resources Board has collected

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*In some cases it may be acceptable to neglect the interference. In other cases, SO_2 or NO_2 data from a nearby site may be used to make the interference correction.

Table 2.4 Number of Hourly SO_2 Readings at SCAB and SEDAB Sites by Year (Hundreds of Measurements)

Site (Station Number)	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975
LOS ANGELES COUNTY										
Azusa (60)	--	--	--	--	62	85	83	87	87	86
Burbank (69)	83	83	83	81	85	83	86	85	86	86
Lennox (76)	83	82	82	83	84	85	83	86	87	86
Long Beach (72)	84	84	84	80	81	84	82	86	86	85
Los Angeles (1)	82	82	83	80	83	84	83	83	85	85
Newhall (81)	--	--	--	--	--	--	20	85	86	86
Pasadena (79) (83)	--	--	20	84	84	86	34 --	85	85	86
Pomona (75)	82	83	84	84	84	85	87	87	87	87
Reseda (74)	83	83	85	84	83	86	86	87	87	87
West LA (71)	83	83	83	83	83	85	85	86	86	84
Whittier (80)	--	--	--	--	--	12	82	85	84	85
ORANGE COUNTY										
Anaheim (377)	83	83	71	84	79	83	86	83	80	80
La Habra (378)	--	34	78	70	76	84	84	86	82	80
RIVERSIDE COUNTY										
Riverside (326)	26	55	67	67	52	43	49	21	38	47
Indio	--	--	--	--	--	--	45	--	--	--
Banning	--	--	--	--	--	--	--	--	64	69
SAN BERNARDINO COUNTY										
Redlands (365)	--	--	--	--	--	--	--	--	--	--
San Bernardino (351)	35	44	63	57	56	71	82	85	85	81

Table 2.5 Number of Hourly NO_2 Readings at SCAB and SEDAB Sites by Year (Hundreds of Measurements)

Site (Station Number)	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975
LOS ANGELES COUNTY										
Azusa (60)	77	77	76	79	73	80	81	81	83	80
Burbank (69)	77	77	76	78	77	78	85	85	83	82
Lennox (76)	74	75	74	77	81	80	83	83	83	82
Long Beach (72)	73	75	75	78	81	81	82	81	79	78
Los Angeles (1)	78	78	76	74	79	80	82	77	80	80
Newhall (81)	--	--	--	--	27	81	81	82	82	83
Pasadena (79) (83)	--	--	31	80	79	81	33 51	84	81	82
Pomona (75)	76	76	78	79	79	81	82	84	83	83
Reseda (74)	77	76	76	77	78	79	83	85	84	84
West LA (71)	78	76	78	81	80	79	80	82	82	81
Whittier (80)	--	--	--	29	79	81	83	81	81	83
Lancaster (82)	--	--	--	--	--	76	83	80	82	83
ORANGE COUNTY										
Anaheim (377)	54	67	74	80	74	79	80	73	80	76
La Habra (370)	--	12	63	59	81	76	79	79	78	78
RIVERSIDE COUNTY										
Riverside (326)	69	67	--	--	--	54	54			
Rubidoux (344)							28	85	82	82
Banning (333) (350)	--	--	--	--	--	52	--	-- --	--	--
Indio (345)	--	--	--	--	--	52	80	84	83	79
Palm Springs (331)	--	--	--	--	--	47	82	85	84	5

Table 2.5 Number of Hourly NO_2 Readings at SCAB and SEDAB Sites by Year (Cont.)

Site (Station Number)	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975
SAN BERNARDINO COUNTY										
Redlands (365)	--	--	49	44	64	75	74	81	77	42
San Bernardino (351)	59	62	58	31	38	66	69	75	81	80
Victorville (369)	--	--	--	--	--	--	--	18	79	81

Table 2.6 Monitoring Methods in the SCAB and SEDAB

Site (Station No.)		Oxidant/Ozone(a)	NO_x(b)	Hydrocarbons(c)
LOS ANGELES COUNTY				
Azusa	(60)	KI (unbuf)	colorimetric (NO)	FI
Burbank	(69)	KI (unbuf)	colorimetric (NO)	FI
Lennox	(76)	KI (unbuf)	colorimetric (NO)	GC/FI
Long Beach	(72)	KI (unbuf)	colorimetric (NO)	--
Los Angeles	(1)	KI (unbuf)	colorimetric (NO)	FI
Newhall	(81)	KI (unbuf)	colorimetric (NO)	FI
Pasadena	(79)	KI (unbuf)	colorimetric (NO)	FI
	(83)	KI (unbuf)	colorimetric (NO)	FI
Pomona	(75)	KI (unbuf)	colorimetric (NO)	FI
Reseda	(74)	KI (unbuf)	colorimetric (NO)	GC/FI
West LA	(71)	KI (unbuf)	colorimetric (NO)	--
Whittier	(80)	KI (unbuf)	colorimetric (NO)	FI
ORANGE COUNTY				
Anaheim	(377)	KI (neut. buf.) prior to 6/1/75, UV photometric calibration since	colorimetric (NO_x)	FI
La Habra	(378)	KI (neut. buf.) prior to 6/1/75, UV photometric calibration since	colorimetric (NO_x)	--
SAN BERNARDINO COUNTY				
Redlands	(365)	KI (neut. buf.) to Jan., 73, chemiluminescent since	colorimetric (NO_x)	--
San Bernardino	(351)	KI (neut. buf.) to June, 73, chemiluminescent since	colorimetric (NO_x)	FI

Table 2.6 Monitoring Methods in the SCAB and SEDAB (Cont'd)

Site (Station No.)		Oxidant/Ozone
LOS ANGELES COUNTY		
Lancaster	(82)	KI (unbuf)
RIVERSIDE COUNTY		
Banning	(333) (350)	KI (neut. buf.) to Jan. 73, UV photometric calibration since
Indio	(345)	KI (neut. buf.) to June 75, UV photometric calibration since
Palm Springs	(331)	KI (neut. buf.) to Jan. 75, UV photometric calibration since
SAN BERNARDINO COUNTY		
Victorville	(369)	KI (neut. buf.) to 1974, chemiluminescent since

(a) KI = potassium iodide, colorimetric method of total oxidant measurement.
KI (Neut. buf.) - KI method, calibrated using neutral buffered KI solution; (ARB's pre-1975 technique).
KI (unbuf.) = KI method, calibrated using unbuffered KI solution; (Los Angeles APCD's past and present technique).
UV photometric calibration = KI method but calibrated using UV photometry, an ozone-specific technique.
Chemiluminescent = measurement of light emitted from ethylene-ozone reaction, believed to be ozone-specific.

(b) (NO) indicates that NO and NO_2 are measured; recorded $NO_x = NO + NO_2$.
(NO_x) indicates that NO and NO_2 are measured; recorded $NO = NO_x - NO_2$.

(c) FI = flame ionization detection, which responds to carbon atoms.
GC/FI = flame ionization detector fed by a gas chromatograph separator column.

the data from the counties, and all the hourly data (with the exception of methane measurements) are available on magnetic tape from the ARB for the years 1963 to 1975. The methane measurements for Los Angeles County (as well as all other Los Angeles County data) are available from the Southern California APCD for the years 1955 to 1975. Technology Service Corporation's aerometric data bank presently includes all of the ARB tapes from 1965 to 1974 and all of the Los Angeles County data from 1955 to August 1974.

2.1.5 Monitor Locations

Figure 2.1 illustrates the geographical location of potential source sites (see Table 2.1) and potential receptor sites (see Tables 2.2 and 2.3). Each open or solid circle in Figure 2.1 represents a potential receptor site. The solid dots could also be used as source sites. It should be noted that every station which provided enough precursor data to qualify as a source site also provided enough oxidant/ozone data to quality as a receptor site.

2.2 METEOROLOGICAL DATA

The meteorological data of most interest in the empirical modeling analysis are wind speed, wind direction, temperature, mixing heights (or other vertical profile data), solar radiation, and relative humidity. The purpose of this section is to document, for the years 1966 through 1975, which SCAB and SEDAB stations have measured and recorded these data in a usable format. The sites examined include meteorological stations as well as combined air quality and meteorological monitors.

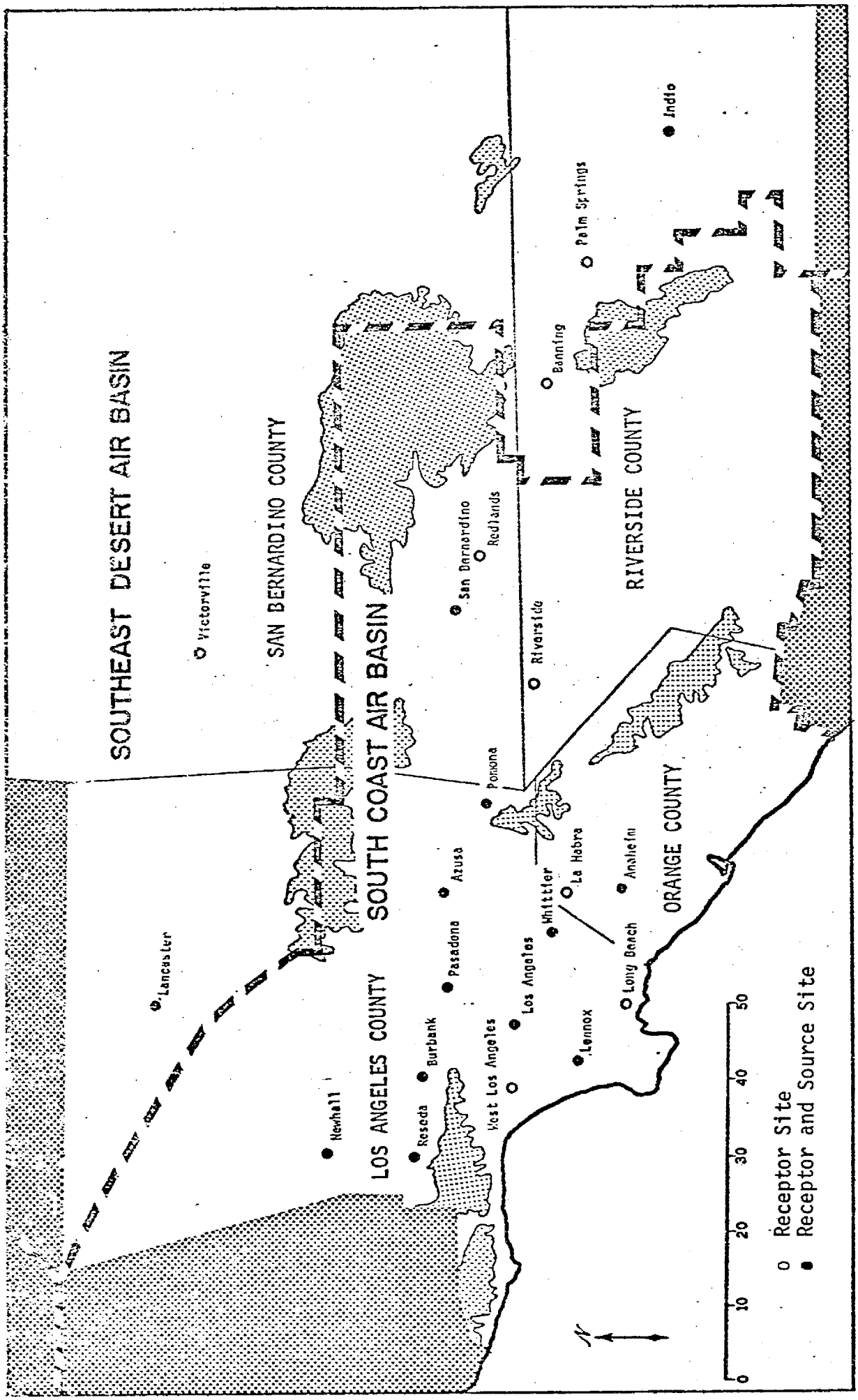

Figure 2.1 Potential Source and Receptor Sites for Empirical Modeling of the Oxidant/Precursor Relationship.

Due to the expense and fragility of the equipment, solar radiation has been measured continuously at only two sites in the Los Angeles area: Downtown Los Angeles (DOLA) and Los Angeles International Airport (LAX). Hourly insolation data for these two sites are available for the years 1956 through 1974. Currently, however, no pyrheliometers are being operated by either the local APCD's or the airports. The two sites at where insolation was measured are mapped in Figure 2.2.

Figure 2.2 also shows the locations of sites at which hourly temperature readings have been recorded. These sites are listed in Table 2.7, along with the number of readings taken per day and the years for which temperature data are available. In addition to the stations listed in Table 2.7, there are numerous other sites, including virtually all of the wind and air quality monitoring facilities, which record the daily maximum and/or minimum temperature.

Because of the importance of pollutant transport, the most important meteorological variables in the present study are wind speed and direction. Figure 2.3 is a map of the 24-hour wind velocity stations in Los Angeles County; Figure 2.4 shows the locations of all wind velocity stations in the SCAB and SEDAB. The station numbers in Figure 2.4 are those of the wind stations, not the corresponding air monitoring stations. Table 2.8 summarizes the availability of meteorological data from each wind monitor location. Note that the majority of these stations record only wind data, although several of the airports and air quality monitoring stations report temperature, visibility, cloud cover, and other data as well.

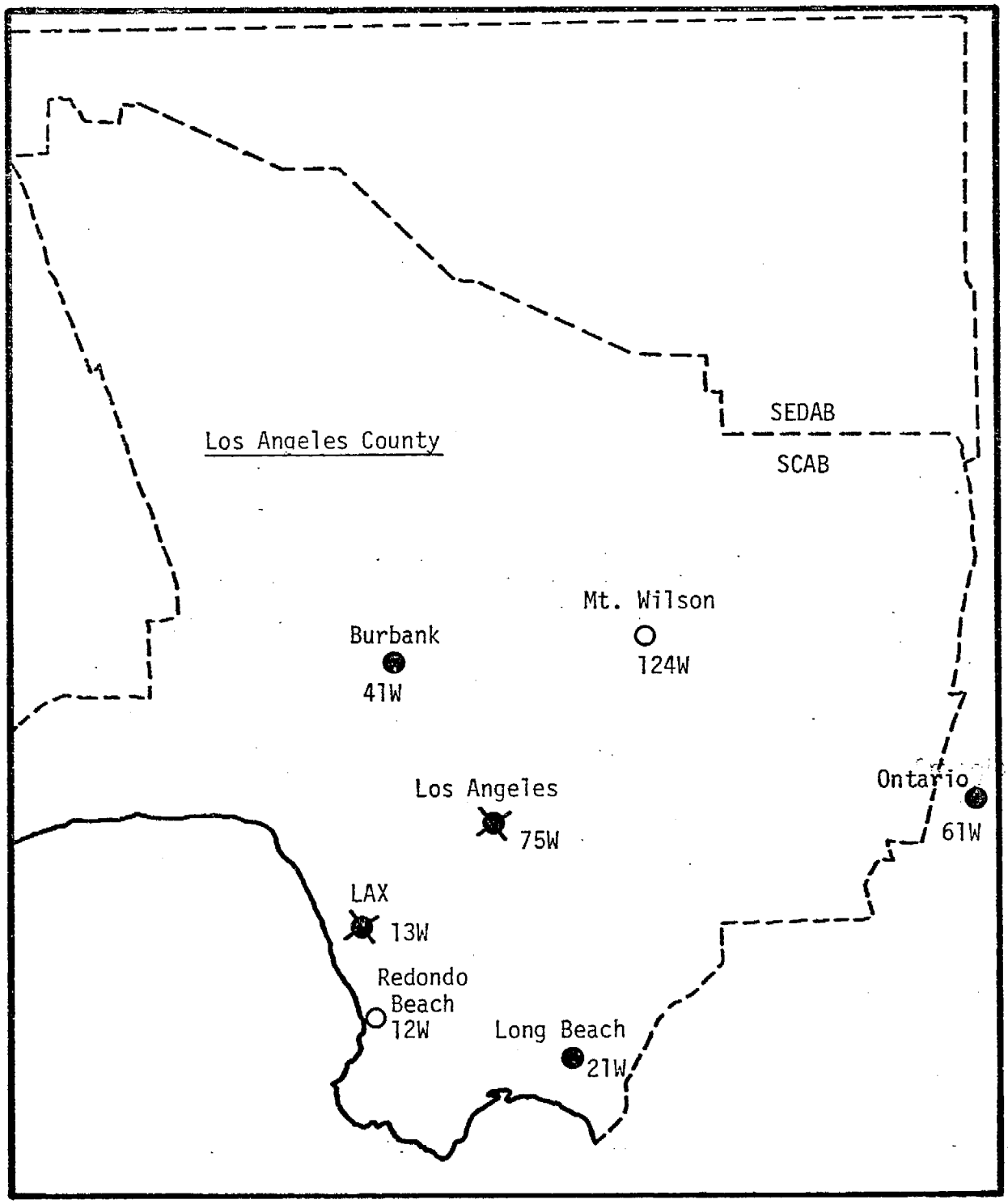

Figure 2.2. Solar Radiation and Temperature Monitor Sites in Los Angeles County[5]

o temperature - 3 hours per day
● temperature - 24 hours per day
✕ temperature - 24 hours per day plus solar radiation - 14 hours per day

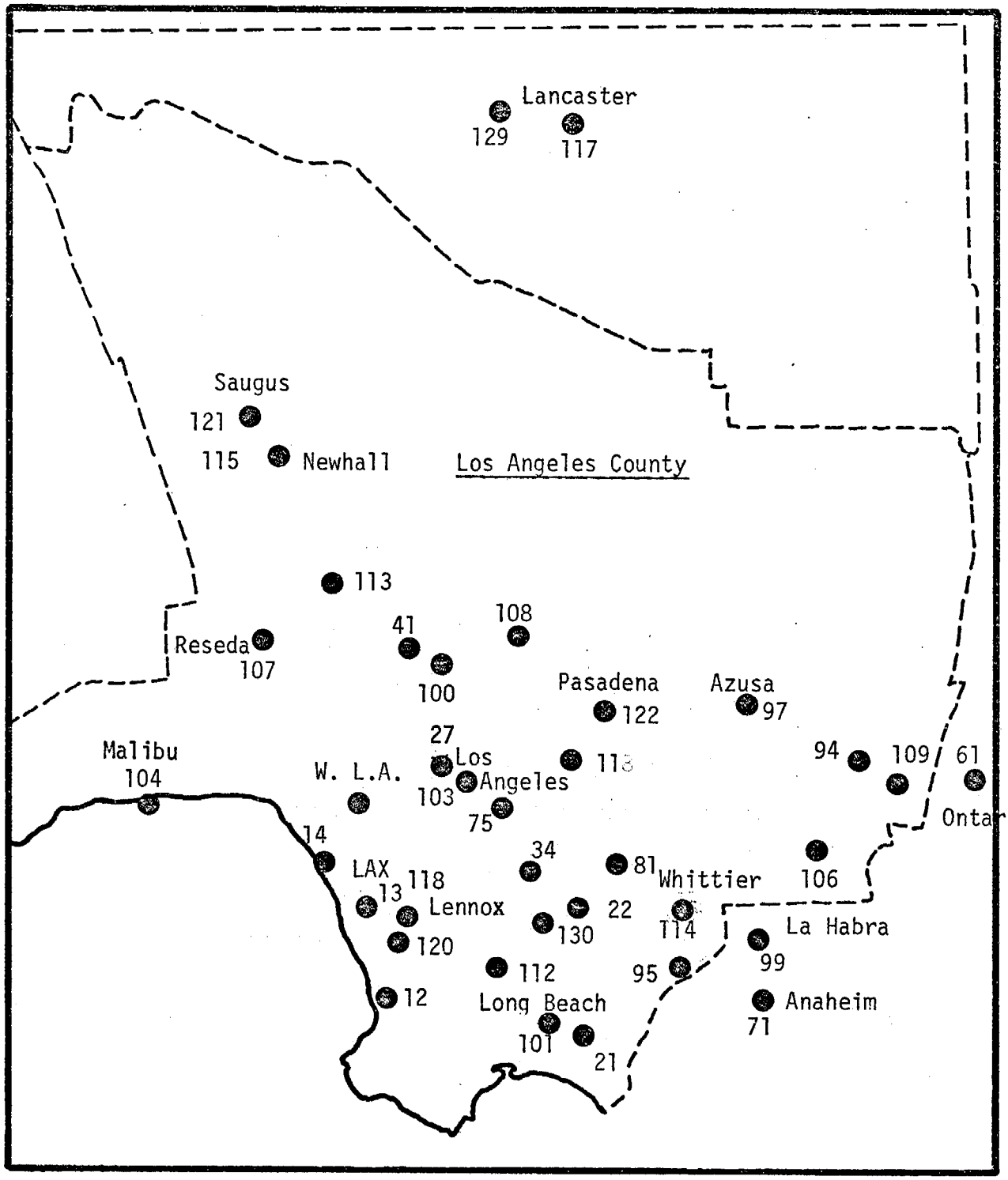

Figure 2.3. Locations of 24-Hour Wind Stations in Los Angeles County[4]

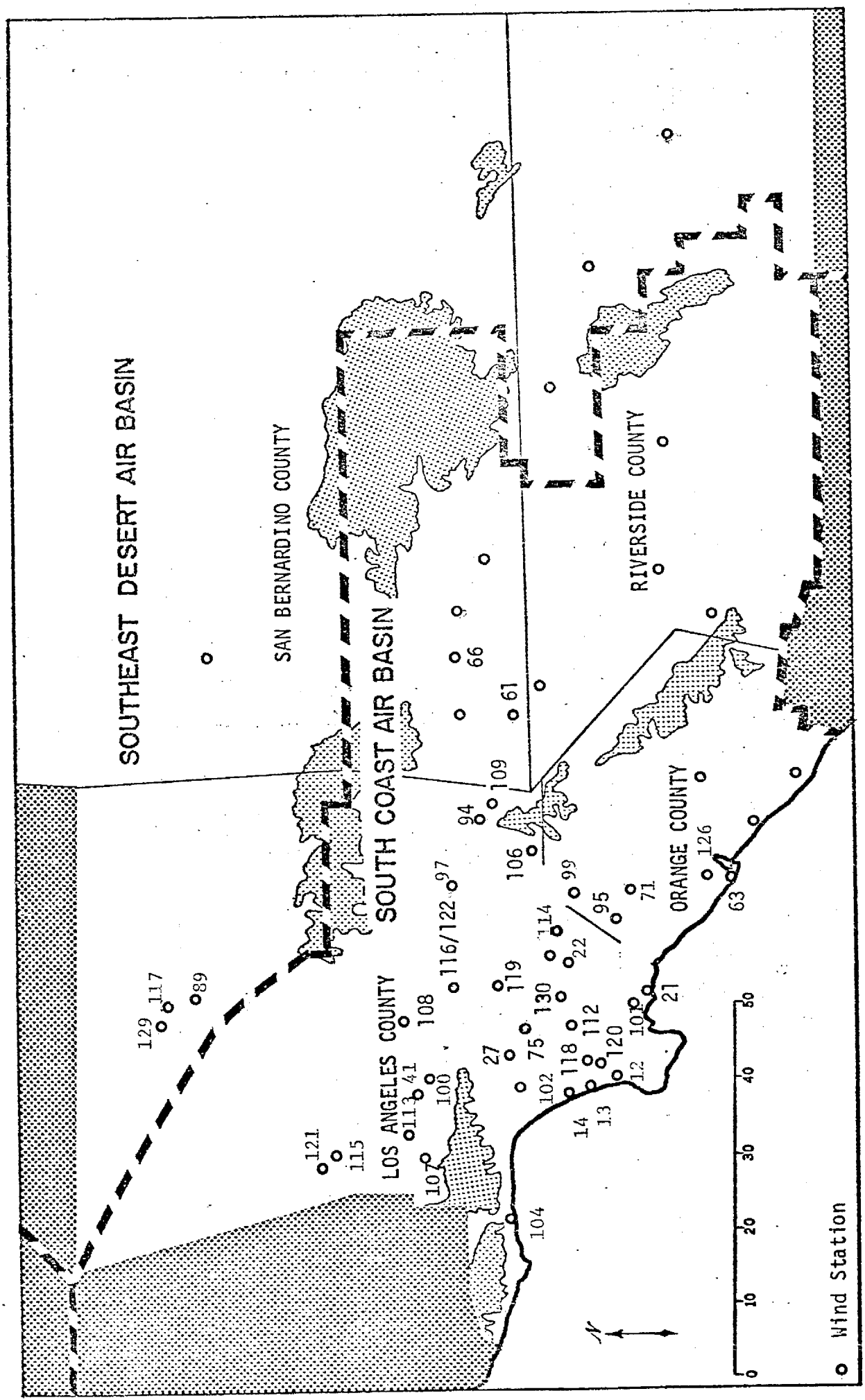

Figure 2.4 Map of Wind Stations in SCAB and SEDAB

Table 2.7 Availability of Hourly Temperature Readings

Site (Meteorological Station No.)	No. of Hourly Readings per Day	Years of Operation
Los Angeles Airport (13 W)	14	1952 - present
Redondo Beach (12 W)	3	1966 - present
Long Beach (21 W)	14	1952 - present
Burbank Airport (41 W)	14	1952 - present
Ontario (61 W)	14	1952 - present
Downtown Los Angeles (75 W)	14	1956 - present
Palmdale (89 W)	14	1952 - 74
Mt. Wilson (124 W)	3	1960 - present

Table 2.8 Meteorological Monitors in SCAB and SEDAB

Site (Meteorological Station No.)	Years of Operation	Punched[b]	Number of Hourly Readings Per Day				
			Wind	Temperature	Visibility	Cloud Cover	Relative Humidity
Los Angeles County							
Zuma Beach (2 W)	1952-	Yes	16	-	-	-	-
Redondo Beach (12 W)*	1966-		24	3	3	3	-
Los Angeles Airport (13 W)	1952-	Yes	24	14	14	-	-
Venice (14 W)*	1954-		24	-	-	-	-
Long Beach Airport (21 W)	1952-	Yes	24	14	14	-	-
Downey (22 W)	1953-		24	-	-	-	-
Hollywood (27 W)	1952-1974		24	-	-	-	-
Vernon (34 W)	1952-		24	-	-	-	-
Burbank Airport (14 W)	1952-	Yes	24	14	14	-	-
Canoga Park (67 W)*	1955-		24	-	-	-	-
Los Angeles Downtown* (75W) [a,c]	1956-	Yes	24	14	9	10	-
Rivera (81 W) *	1956-		24	-	-	-	-
Palmdale Airport (89 W)	1952-1974	Yes	24	14	14	-	-
Brackett Airport (94 W)*	1958-		24	-	-	-	-

Table 2.8 Meteorological Monitors in SCAB and SEDAB (Cont.)

Site (Meteorological Station No.)	Years of Operation	Punched[b]	Number of Hourly Readings Per Day				
			Wind	Temperature	Visibility	Cloud Cover	Relative Humidity
Azusa (97 W)[(a)]*	1960-		24	-	-	-	-
Lancaster (98 W)*	1960-1974		24	-	-	-	-
Lancaster (129 W)*	1974-		24	-	-	-	-
Burbank (100 W)[(a)]*	1962-		24	-	-	-	-
Long Beach (101 W)[(a)]*	1962-		24	-	-	-	-
West LA (102 W)[(a)]*	1962-		24	-	-	-	-
Los Angeles College* (103 W)	1963-		24	-	-	-	-
Malibu (104 W)*	1963-		24	-	-	-	-
Walnut (106 W)*	1965-		24	-	-	-	-
Reseda (107 W)[(a)]*	1965-		24	-	-	-	-
La Canada (108 W)*	1965-		24	-	-	-	-
Pomona (109 W)[(a)]*	1965-		24	-	-	-	-
Compton (112 W)*	1966-		24	-	-	-	-
Whittier (114 W)[(a)]*	1969-		24	-	-	-	-
Newhall (115 W)[(a)]*	1969-		24	-	-	-	-
Pasadena (116 W)[(a)]*	1970-1972		24	-	-	-	-
Pasadena (122 W)[(a)]*	1972-		24	-	-	-	-

Table 2.8 Meteorological Monitors in SCAB and SEDAB (Cont.)

Site (Meteorological Station No.)	Years of Operation	Punched[b]	Number of Hourly Readings Per Day				
			Wind	Temperature	Visibility	Cloud Cover	Relative Humidity
Lancaster (117 W)[(a)]*	1970-		24	-	-	-	-
Lennox (118 W)[(a)]*	1971-		24	-	-	-	-
Alhambra (119 W)*	1970-		24	-	-	-	-
Hawthorne (120 W)*	1970-		24	-	-	-	-
Saugus (121 W)	1971-		24	-	-	-	-
Lynwood (130 W)*	1973-		24	-	-	-	-
Orange County							
Newport Beach (63 W)	1954-		24	2	2	2	-
Amaheim (71 W)[(a)]*	1958-		24	-	-	-	-
Buena Park (95 W)*	1959-		24	-	-	-	-
La Habra (99 W)[(a)]*	1960-		24	-	-	-	24
Costa Mesa (126 W)[(a)]*	1972-		24	-	-	-	-
Los Alamitos (127 W)[(a)]*	1972-		24	-	-	-	24
Santa Ana Canyon[(a,c)]	1974-		24	-	-	-	24
El Toro[(a,c)]	1973-		24	-	-	-	24
Laguna Beach[(a,c)]	1974-		24	-	-	-	24

Table 2.8 Meteorological Monitors in SCAB and SEDAB (Cont.)

Site (Meteorological Station No.)	Years of Operation	Punched[b]	Number of Hourly Readings Per Day				
			Wind	Temperature	Visibility	Cloud Cover	Relative Humidity
Riverside County							
Prado Park[(c)]	1971-		24	-	-	-	-
Riverside[(a,c)]	1965-1972		24	-	-	-	-
Riverside[(a,c)]	1972-		24	-	-	-	-
Perris[(a,c)]	1973-		24	-	-	-	-
Elsinore[(a,c)]	1974-		24	-	-	-	-
Temecula[(a,c)]	1974-		24	-	-	-	-
Hemet[(a,c)]	1972-		24	-	-	-	-
Banning[(a,c)]	1973-		24	-	-	-	-
Palm Springs[(a,c)]	1971-		24	-	-	-	-
Indio[(a,c)]	1971-		24	-	-	-	-
San Bernardino County							
Ontario Airport (61 W)	1952-	Yes	24	14	14	-	-
Fontana (66 W)	1953-		24	-	-	-	-
Upland[(a,c)]	1972-		24	-	-	-	-
Chino[(a,c)]	1974-		24	-	-	-	-

Table 2.8 Meteorological Monitors in SCAB and SEDAB

Site (Meteorological Station No.)	Years of Operation	Punched[b]	Number of Hourly Readings Per Day				
			Wind	Temperature	Visibility	Cloud Cover	Relative Humidity
San Bernardino[a,c]	1963-		24	-	-	-	-
Redlands[a,c]	1968-1973		24	-	-	-	-
Yucaipa[a,c]	1974-		24	-	-	-	-
Lake Gregory[a,c]	1974-		24	-	-	-	-
Big Bear[a,c]	1974		24	-	-	-	-

[a] Also an air quality monitor.

[b] Yes entries indicate data are available on punched cards, magnetic tape, or other digital format.

[c] Not part of Los Angeles county met. station network; hence, no station number.

* See Section 4.3 for discussion.

Note also that the data are available in punched form or on magnetic tape from only a few of the sites.

Relative humidity is or has been measured at most sites within Los Angeles and Orange counties. Unfortunately, humidity data are no longer collected at the Los Angeles county sites due to the unreliability and obsolescence of the instruments.[5] Therefore, humidity data are available only for the Orange County air monitoring sites, as indicated in Table 2.8.

Low-level soundings have been taken twice per day at Los Angeles Airport (LAX) and at El Monte Airport (EMT) since mid-1971. Unfortunately, these are the only two sites in the SCAB for which long-term daily or twice-daily inversion data are available.* To the extent that the inversion height is nearly uniform with a moderate west-to-east gradient, this may not be a serious limitation. Also, the surface air temperature at Mt. Baldy and other high-altitude sites correlates well with the temperature aloft; these temperatures can be used to estimate the strength of the inversion layer.[6]

To summarize, this section has demonstrated that reasonably complete wind data are available, although mostly in the form of printed sheets instead of punch cards or magnetic tape. Temperature data are available at a few locations. Relative humidity data are essentially unavailable for the recent years of interest (except for Orange County). Solar radiation and inversion height data are available at only two stations each.

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*"Maximum inversion height" is reported for the downtown Los Angeles station each day, but this is a computed, not a measured, quantity.

2.3 REFERENCES

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6. Bennett, C., California Air Resources Board, personal communication, November 1976.

3.0 SELECTION OF POTENTIAL PRECURSOR AND RECEPTOR AREAS

During the time between the onset of photochemical reactions in the morning and the attainment of maximal oxidant levels in the afternoon, a given parcel of air can travel many miles. The hydrocarbons and oxides of nitrogen released at one location, the "source area," will generate oxidant at other sites, the "receptors," further downwind. The empirical modeling analysis will account for the movement of air parcels from source areas to receptor areas by using wind trajectories constructed from local wind field data.

Naturally, actual source areas and receptor areas vary from day to day depending upon the local wind field. However, the daytime wind flow of the Los Angeles Basin during the June to October smog season is dominated by a single general pattern. The empirical modeling study will concentrate on days exhibiting this common wind flow, excluding days with other patterns. This will allow transport to be included in the study while maintaining a sufficiently large data base for the statistical analysis.

The objective of this chapter is to describe the prevailing wind flow patterns in the Los Angeles Basin and to identify general source/receptor areas appropriate to the most common pattern. Subsequent phases of this project will select specific dates for the empirical analysis and specific monitoring sites within the general source/receptor areas. The selection of dates will be based on daily wind field data, while the selection of specific sites will be based on both wind field data and tests of which sites (or groups of sites) provide the best statistical fit between precursors and oxidant.

3.1 PREVAILING WIND PATTERNS

Figures 3.1 through 3.3 illustrate the three most prevalent classes of streamflow patterns in the Los Angeles Basin, as identified by the California Air Resources Board.[1] These three patterns, "west," "diurnal south," and "east," account for more than 75% of the hourly streamflow patterns observed each year. The west pattern alone accounts for 41% of all windflows during the year.

Table 3.1 presents the frequency of occurrence of each type of pattern for the four quarters of the year and at four times of day. Table 3.1 demonstrates that the west and south flows predominate during daytime periods (10 AM and 4 PM). This represents the persistent daily sea breeze in the Los Angeles area. The east flow, which is common at night and on some winter days, represents a land breeze or drainage flow of air out of the basin.

The empirical modeling study will relate afternoon oxidant to early morning precursors during the smog season. Thus, the transport phenomenon of most interest is the one which occurs during daylight hours in the third quarter of the year (July through September). Table 3.1 reveals that the westerly pattern dominates this time of interest, although a southerly flow often occurs during the earliest hours of the day. Accordingly, we will select the source and receptor areas based on the dominant westerly pattern, taking into account a secondary southerly component.

The conclusions of the ARB wind flow summary[1] are substantiated by other studies of both streamlines and wind trajectories (see reference list). For example, Figure 3.4 presents a map of wind streamlines

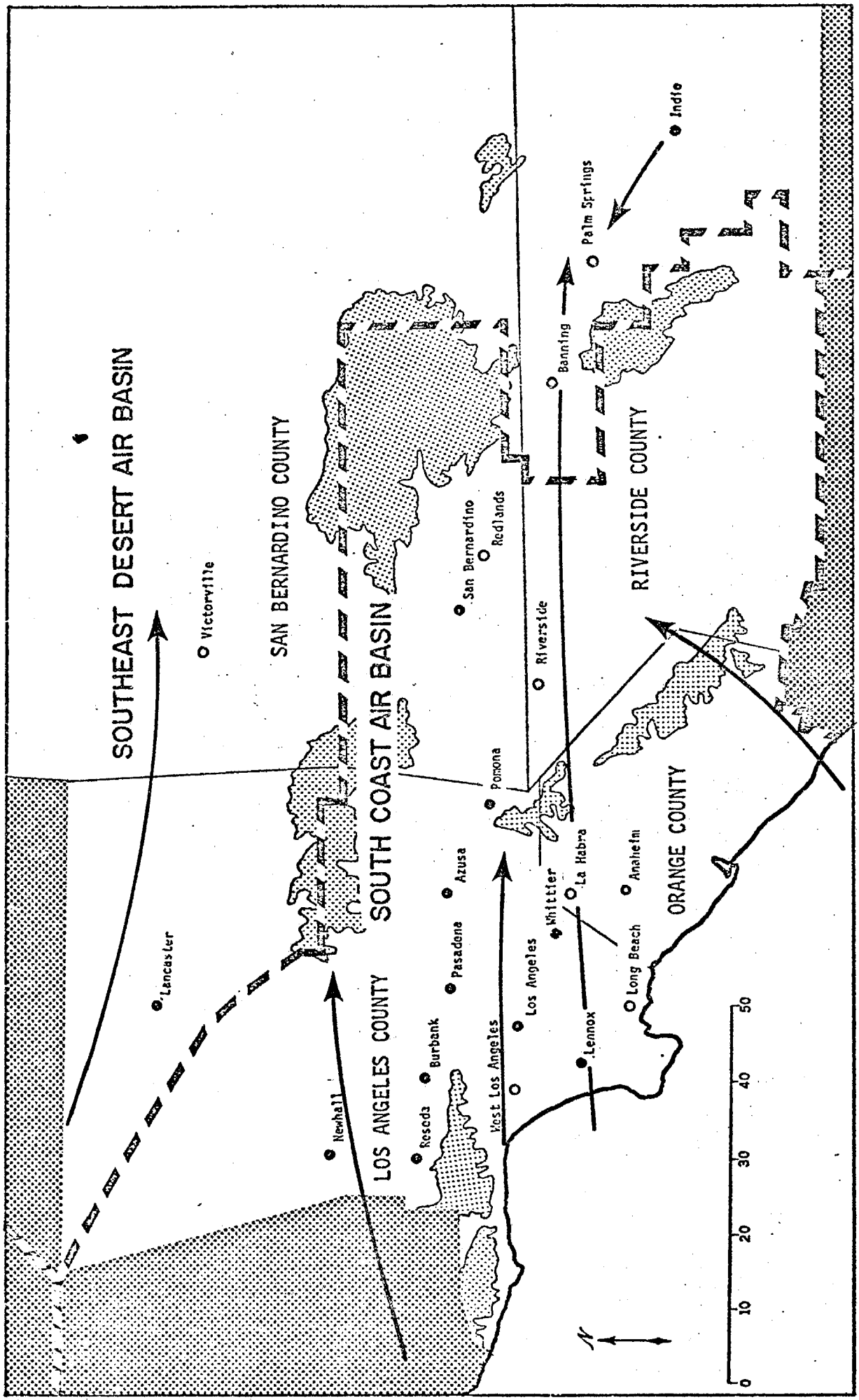

Figure 3.1 Streamlines for the Westerly Flow Pattern[1].

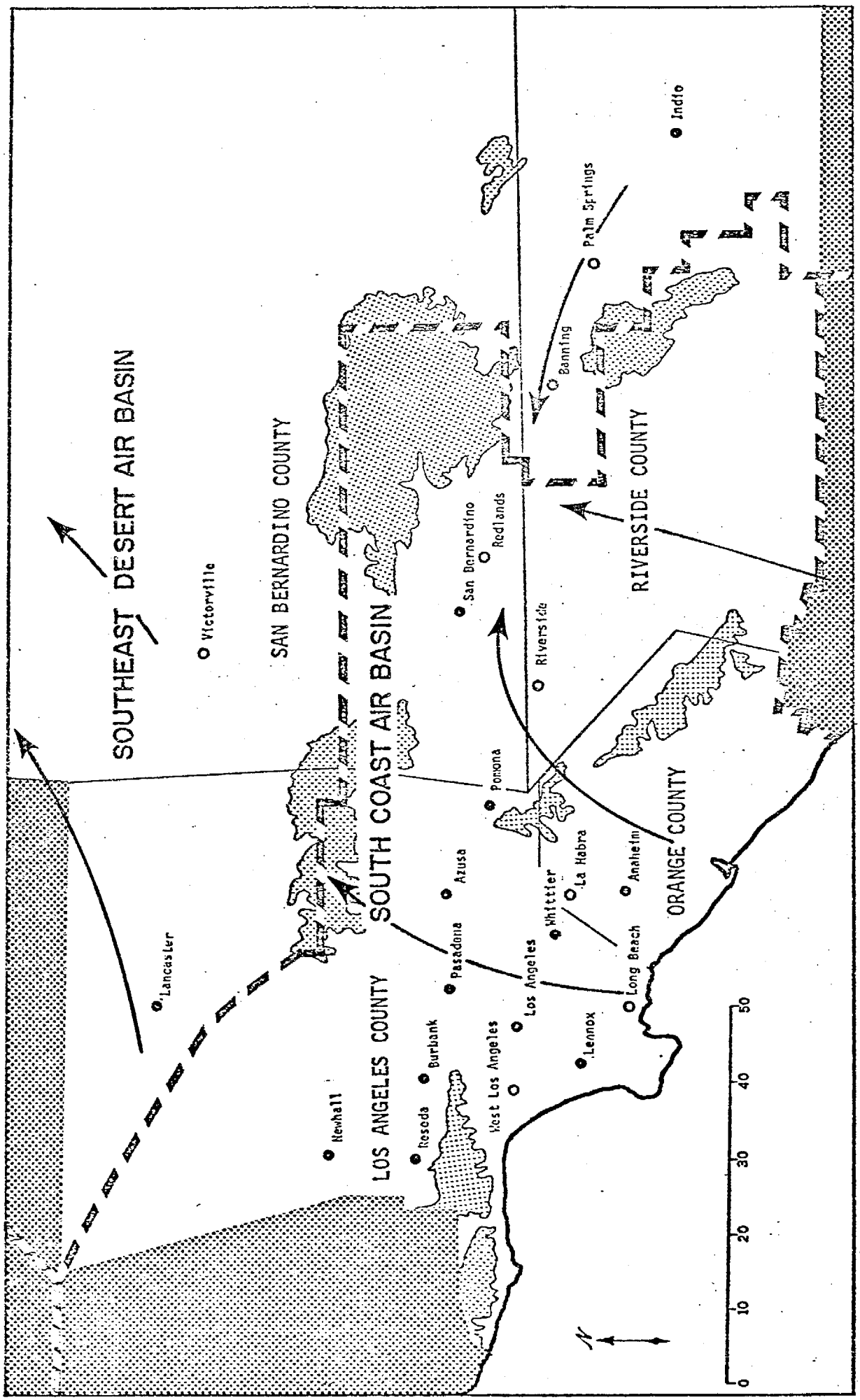

Figure 3.2 Streamlines for the Diurnal South Pattern[1].

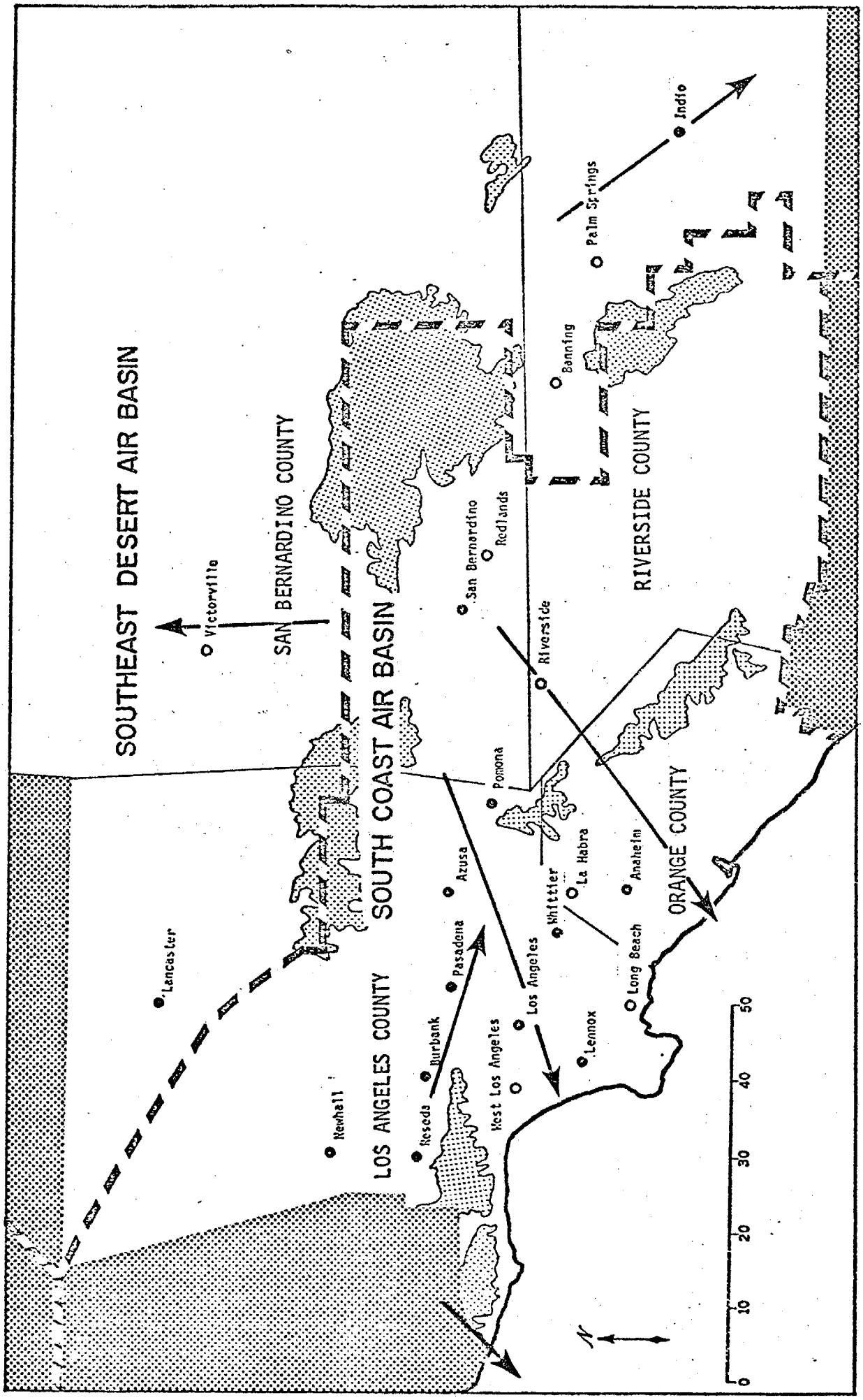

Figure 3.3 Streamlines for the Easterly Wind Flow Pattern[1].

Table 3.1. Percent Occurrence of Air Flow Patterns[1]

SEASON / TIME OF DAY	WEST	SOUTH	EAST	ALL OTHERS
Jan-Mar				
4 AM	15%	11%	37%	37%
10 AM	17	17	27	40
4 PM	50	24	4	21
10 PM	28	12	24	37
Apr-Jun				
4 AM	35%	15%	37%	12%
10 AM	32	44	2	23
4 PM	68	25	1	6
10 PM	60	30	4	6
Jul-Sept				
4 AM	44%	19%	19%	19%
10 AM	43	38	3	18
4 PM	83	13	0	5
10 PM	62	28	5	5
Oct-Dec				
4 AM	20%	5%	44%	29%
10 AM	16	14	26	44
4 PM	47	10	2	42
10 PM	27	3	35	35

This table, based on 1974 and 1975 data, is condensed from Reference 1. The "all others" category comprises five conditions, including "calm" and "Santa Ana," identified by the California Air Resources Board.

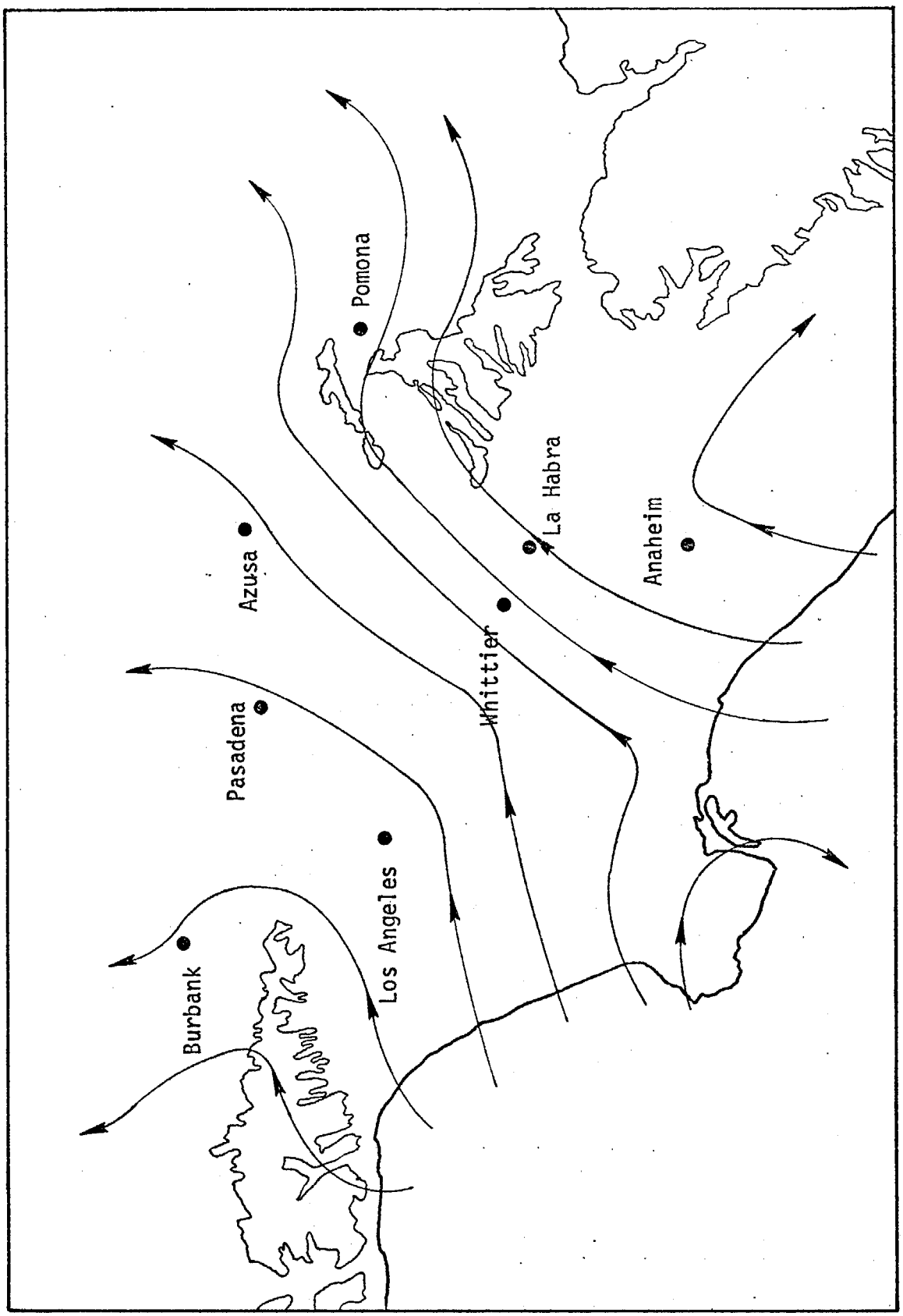

Figure 3.4 Streamlines for 1430 PST, September 22, 1954[2]

identified by researchers in the 1950's.[2] Although streamline maps illustrate the travel of many air parcels at one moment in time while trajectories are "moving pictures" of individual air parcels, the two lead to similar conclusions during periods of stable flow. Other streamline maps (Figure 3.5)[3] and trajectory studies[4-10] bear a strong resemblance to the earlier figures of this chapter.

3.2 SELECTION OF SOURCE AND RECEPTOR SITES

From our analysis of the predominant wind flow patterns, it is possible to identify pairs of monitoring sites such that one site generally lies downwind of the other during the typical daytime flow of the smog season. In many cases, the streamline patterns indicate that two or more source sites may correspond to a single receptor site, or that a single source site may supply two or more receptors. In these instances we have identified site "clusters," where a cluster is a group of adjacent sites, all of which represent a general source or receptor area. In the later phases of this project, weighted averages of the pollutant concentrations among the sites of each cluster will be used in the statistical models. The weighting factors will be selected using a trial-and-error algorithm which seeks the best fit between measured precursor levels and oxidant levels.

Out of the hundreds of possible combinations of source/receptor sites and site clusters, we have selected five source/receptor areas which seem particularly interesting and useful. Our selection criteria included the following:

1. Three to five years of reliable, nearly complete* hydrocarbon and NO_x data must be available at each source site, with

*Chapter 2 discusses data completeness criteria, while Chapters 5 and 6 discuss data quality tests.

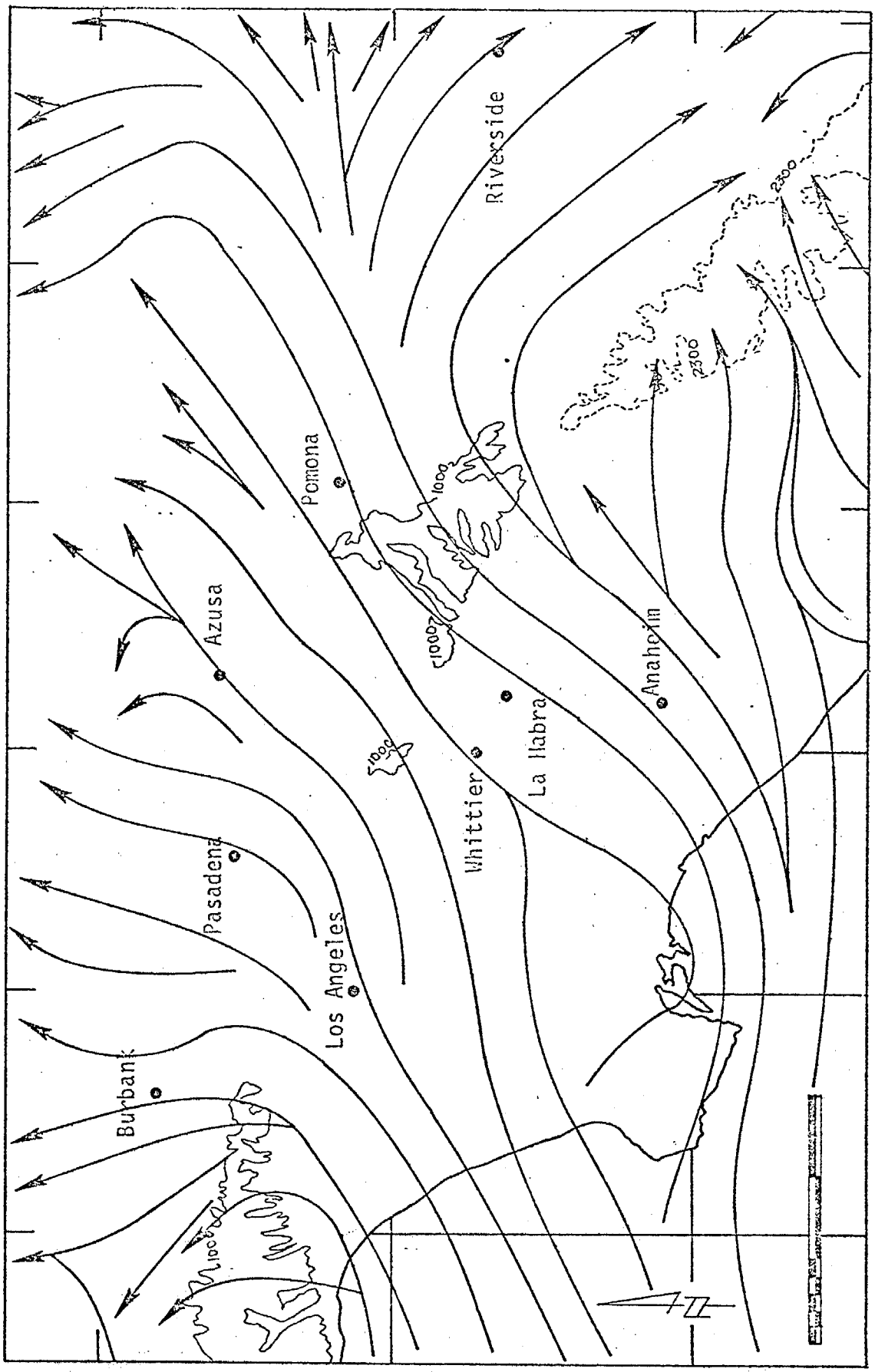

Figure 3.5 Streamlines of Most Frequent Surface Winds During July[3]

corresponding reliable and nearly complete oxidant data available at each receptor site.

2. The source site(s) must lie upwind of the receptor site(s) when the wind follows the predominant daytime pattern of the photochemical smog season (roughly defined as June through October).
3. A variety of transport distances (and associated times of a maximum oxidant occurrence) should be represented among the selected source/receptor pairs.

Based on the above criteria, we have tentatively selected five pairs of source and receptor areas. These are illustrated in Figures 3.6 through 3.10 and are briefly discussed below:

1. SOURCE: Downtown Los Angeles (DOLA)

   RECEPTOR: DOLA

In this case, the same site will be used as both source and receptor. The analysis will be restricted to days with unusually light, variable winds (3 mph or less). On such days, it will be assumed that little transport occurs, and that the oxidant at DOLA at around 11 to 12 AM results from reactions of the morning precursors measured at DOLA. (See Figure 3.6.)

2. SOURCE: DOLA

   RECEPTORS: Burbank, Pasadena, and DOLA

When the prevailing westerly wind pattern occurs, air from DOLA moves along two diverging trajectories, one northward toward Burbank, the other northeast to Pasadena. In this case, the early morning hydrocarbon and NO_x levels at DOLA should correlate with the 11 AM to 1 PM oxidant concentrations at Burbank and Pasadena. This case represents the short-range

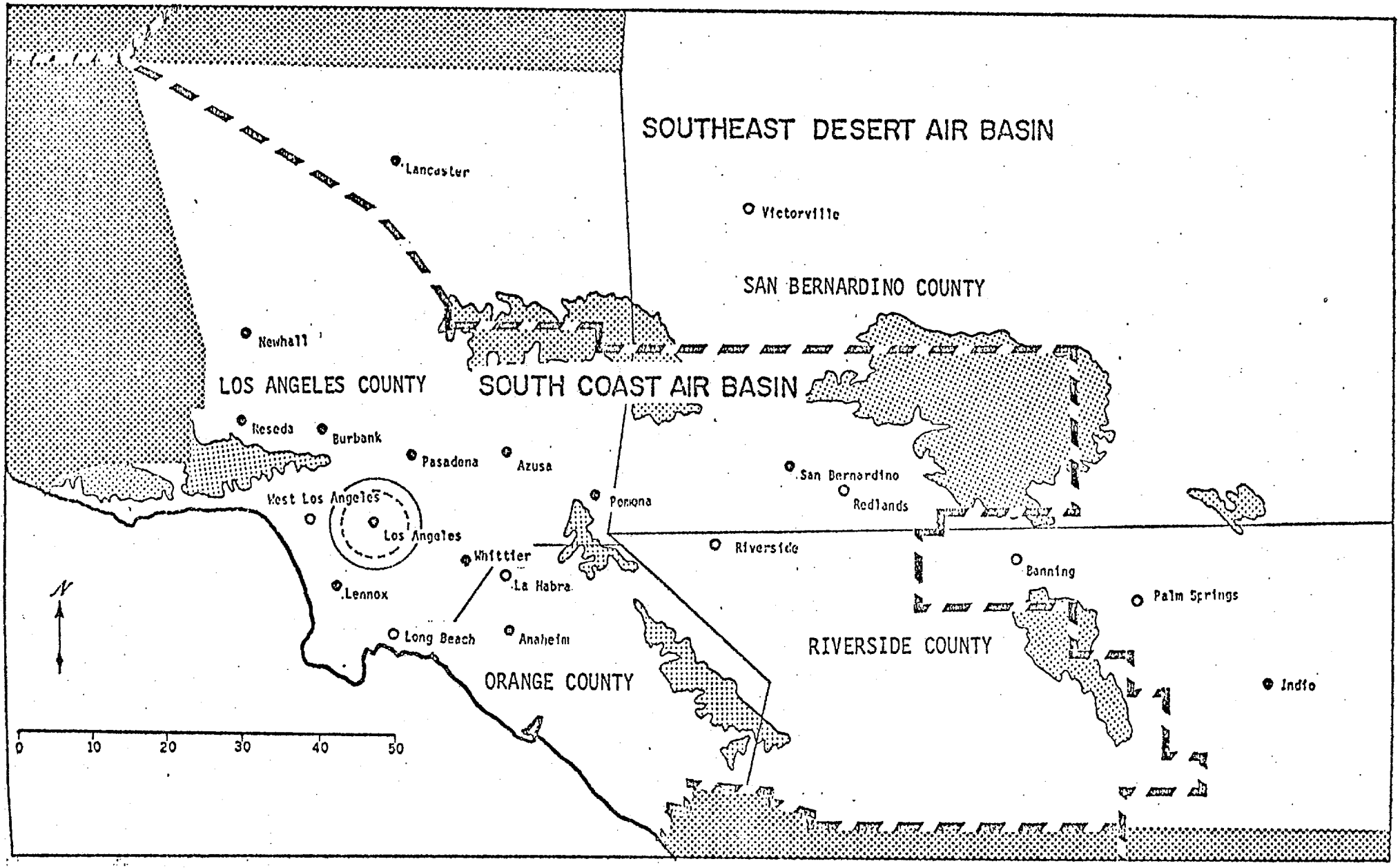

Figure 3.6 Downtown Los Angeles as Both Source and Receptor.

transport of polluted air between adjacent areas of the Los Angeles Basin. When winds are light, DOLA might also be used as a receptor site in this analysis. (See Figure 3.7.)

3. SOURCES: DOLA and Whittier

RECEPTORS: Pomona, Azusa, and Pasadena

This is a medium-range transport study, again to be conducted for days during which the normal westerly wind pattern is present. Because of the greater distances involved here, it takes longer for the precursor-laden air from the source sites to reach the receptors; hence we anticipate that the morning precursor levels at the sources will correlate best with the 1 to 4 PM oxidant levels at the receptors. Because of the particularly high afternoon oxidant concentrations occurring in this receptor area, this case is one of the most important in the study. (See Figure 3.8.)

4. SOURCES: Whittier and Anaheim

RECEPTORS: San Bernardino, Riverside, and Redlands

The typical trajectory reaching these sites is a more southerly one which does not pass through the Los Angeles central business district. Because of the great distance between sources and receptors in this case, the morning precursor levels should correlate best with a late afternoon (3 to 6 PM) oxidant peak. Because of the large horizontal and vertical diffusion which can occur over a 50-mile trajectory, it is anticipated that the correlations found in this portion of the study may be somewhat weaker than those of the earlier parts. (See Figure 3.9.)

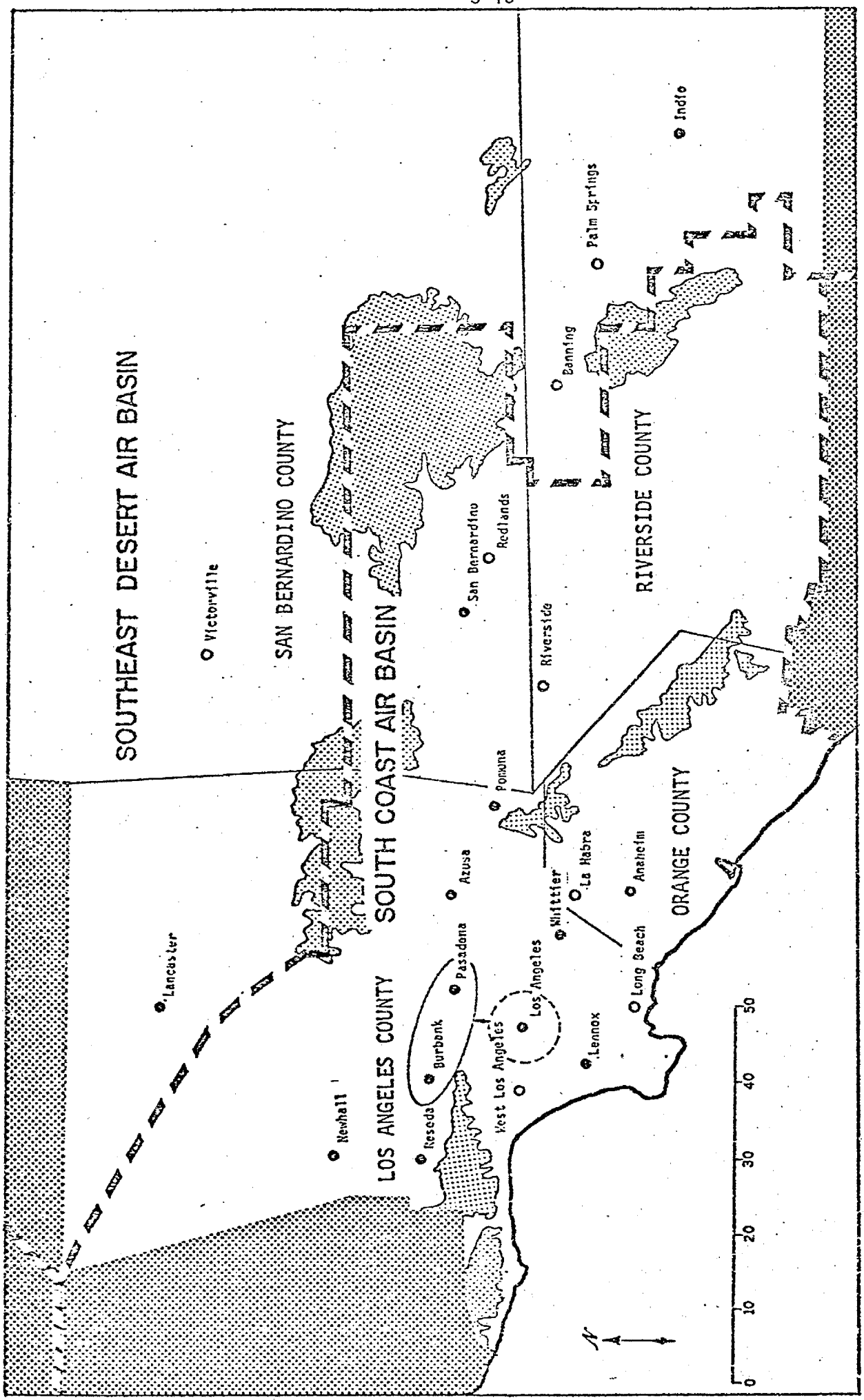

Figure 3.7 Downtown Los Angeles as Source; Burbank and Pasadena as Receptors.

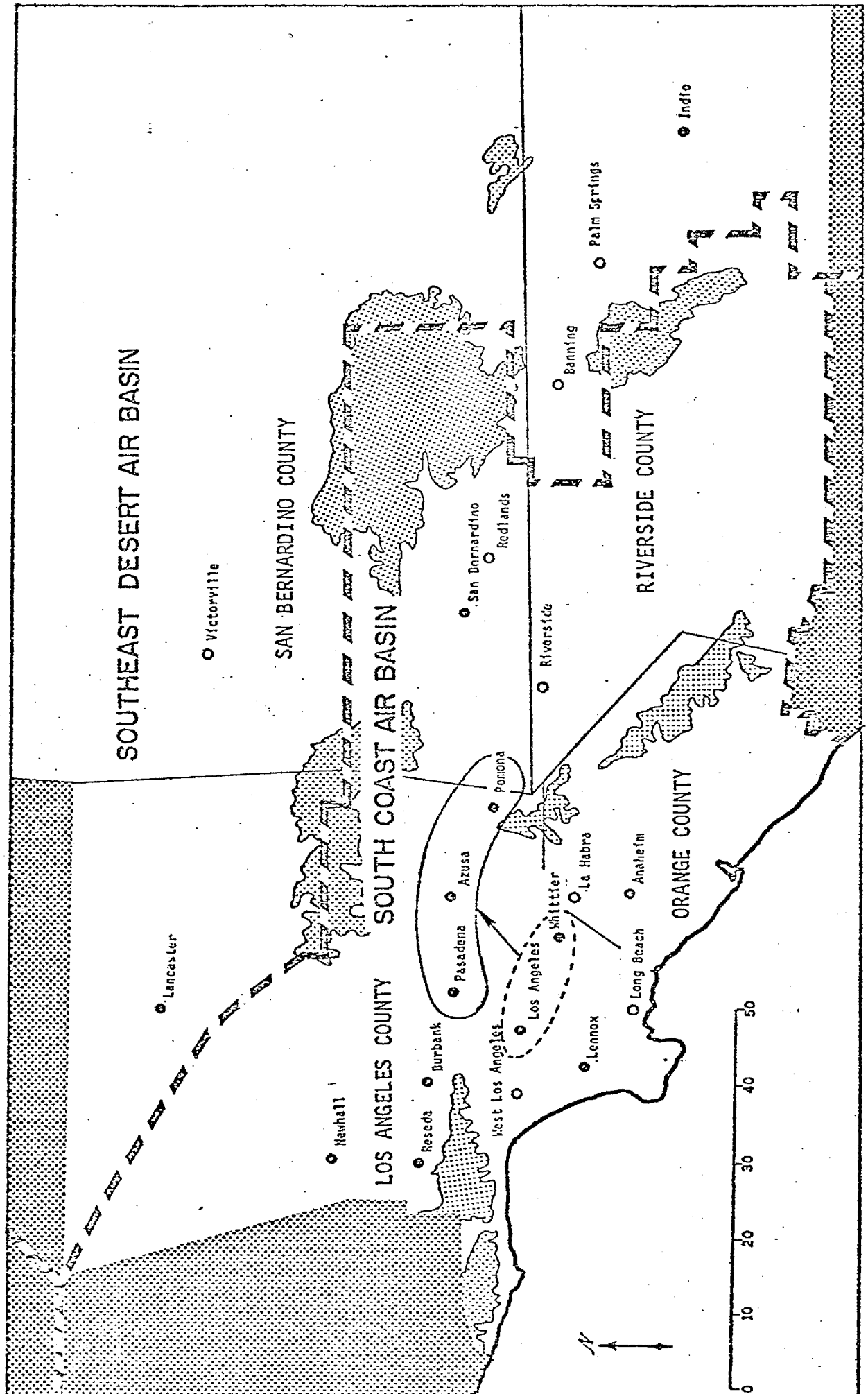

Figure 3.8 Downtown Los Angeles and Whittier as Sources; Pomona, Azusa, and Pasadena as Receptors.

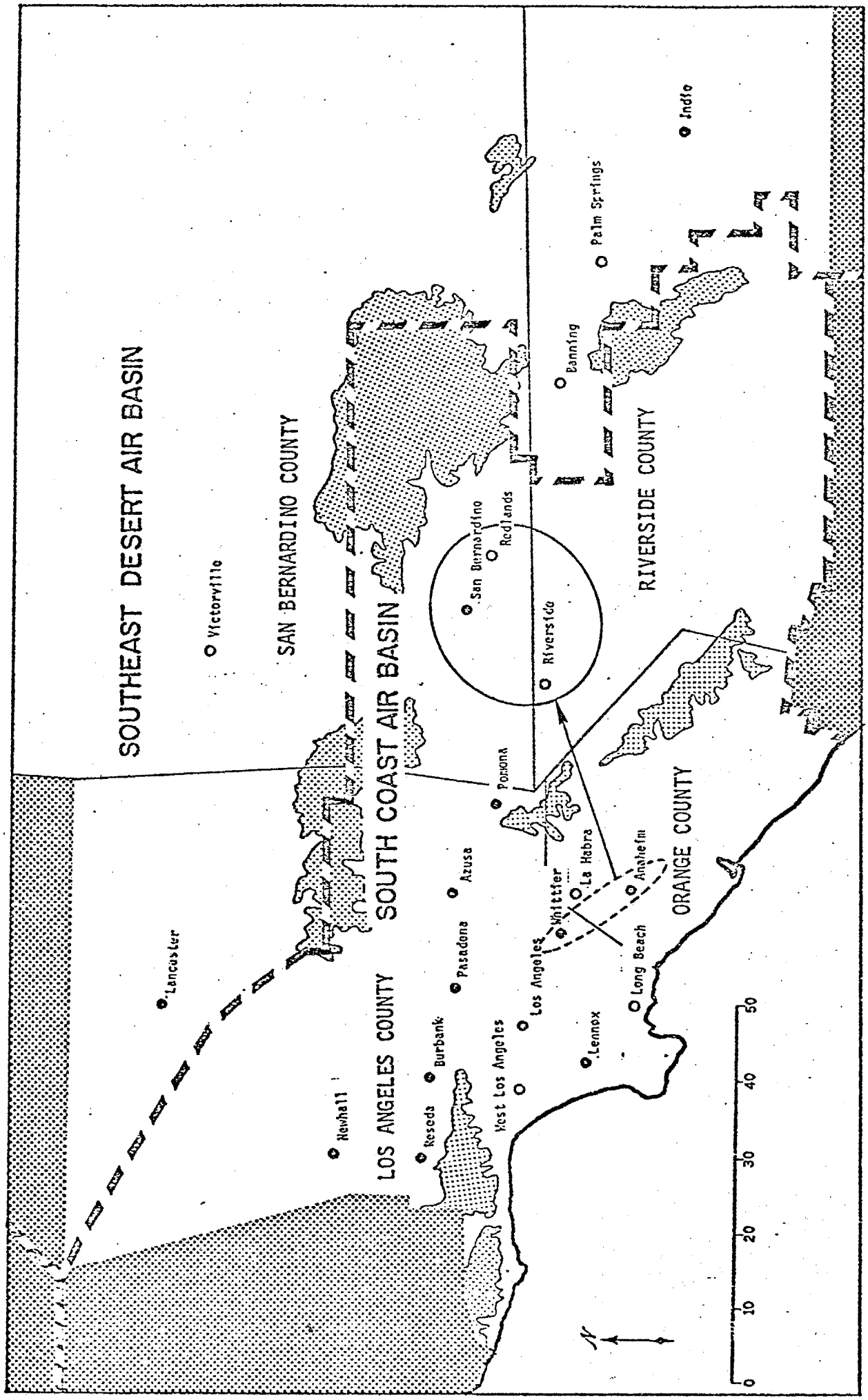

Figure 3.9 Whittier and Anaheim as Sources; San Bernardino, Riverside, and Redlands as Receptors.

5. SOURCES: Pomona, Whittier, Anaheim, DOLA, Azusa, Pasadena, and San Bernardino

RECEPTORS: Banning and Palm Springs

These sites will be used to correlate the overall morning hydrocarbon and NO_x levels of the central-southern Los Angeles Basin against the evening oxidant levels in the inland desert region (the Coachella Valley). Because of the long transport distances involved, we have selected an expansive source region to ensure that the actual source area is represented. Our preliminary statistical analyses may lead to a reduction in the number of source sites. This analysis will be restricted to days with reasonably steady westerly wind patterns throughout the afternoon hours, with a northwesterly flow into the Coachella Valley. In spite of the size of the source area and the carefully restricted set of days to be used in the study, it still may be that precursors from unrepresented source areas, such as southern Orange County and San Diego County, contribute to the oxidant in Palm Springs, thereby interfering with the analysis. (See Figure 3.10.)

Several stations which would have been desirable sources or receptors were omitted from the above list for various reasons, including lack of sufficient data. Many potential source sites had little or no hydrocarbon data. The Lennox station, which lies near the coast and which would have made an interesting source site, is separated from Los Angeles and other potential receptors by oil recovery activities, refining operations, industrial sources, and heavy traffic areas. It was thought that the precursor measurements at Lennox might be unrepresentative of the major source area immediately

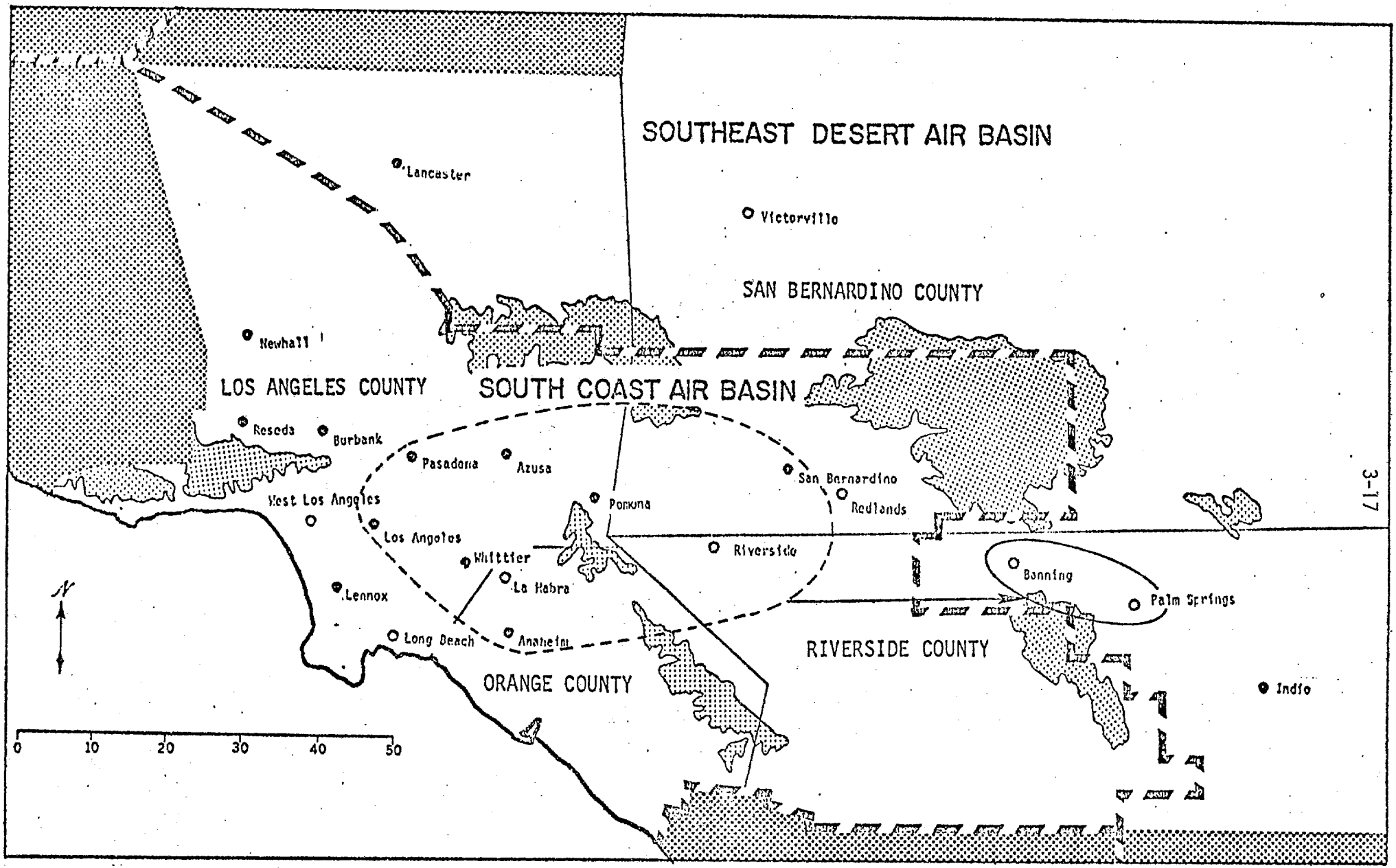

Figure 3.10 Central Los Angeles Basin as Source; Banning and Palm Springs (Coachella Valley) as Receptors.

inland (downwind) from it, and would therefore be unrepresentative of the precursor concentrations associated with the oxidant measured at the receptor sites.

Table 3.2 summarizes the selected source and receptor sites, the distances between them, and the general wind flow patterns to be used. It should be noted that the above selections are tentative, pending review and suggestions by the ARB and EPA project officers. Specific data availability problems or other unforeseen circumstances may also force changes in the site selections during later phases of the project.

Table 3.2. Source--Receptor Pairs for the Statistical Study

PAIR #	SOURCE(S)	RECEPTOR(S)	WIND	TRANSPORT DISTANCE
1	DOLA	DOLA	calm	0 km
2	DOLA	Pasadena, Burbank, DOLA	west	0 - 25 km
3	DOLA, Whittier	Pomona, Azusa, Pasadena	west	15 - 45 km
4	Whittier, Anaheim	San Bernardino, Riverside, Redlands	west	50 - 80 km
5	Pomona, Whittier, Anaheim, Pasadena, DOLA, Azusa, San Bernardino	Banning, Palm Springs	west	50 - 170 km

3.3 REFERENCES

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4.0 REVIEW OF MONITORING METHODS

In assessing the quality of air pollution data, it is important to understand the monitoring techniques which provide the data and the limitations of those techniques. This chapter provides a review of monitoring methods for the pollutants of interest in the empirical modeling study. Section 4.1 describes the monitoring methods in general and discusses interferences, calibration problems, and other sources of error. Section 4.2 summarizes the explicit monitoring practices followed in the South Coast Air Basin. The chapter concludes with a note on potential problems in collecting meteorological data.

4.1 REVIEW OF AIR QUALITY MEASUREMENT METHODS

This section describes several of the analytical methods commonly used to measure ambient concentrations of three groups of air pollutants: 1) total hydrocarbons (HC), methane (CH_4), and nonmethane hydrocarbons (NMHC); 2) nitric oxide (NO), nitrogen dioxide (NO_2), and total oxides of nitrogen (NO_x); and 3) ozone (O_3) and total oxidant (OX). The main objective is to point out some of the differences among monitoring methods and to describe the major interferences and error sources associated with each monitoring method.

4.1.1 Hydrocarbon, Methane, and Nonmethane Hydrocarbon Monitors

Flame ionization detection is used almost universally for HC measurements in the South Coast Air Basin. The basic apparatus consists of a burner, a hydrogen gas (H_2) source, a 100 volt D.C. power supply, and a

set of electrodes with an ammeter. When the sample gas is introduced with the H_2 into the burner, the volatile hydrocarbons present in the sample undergo chemi-ionization and give off carbon ions, which are attracted to the positive electrode near the burner[1]. The current flow between the electrodes is approximately proportional to the concentration of carbon ions present in the flame and is therefore roughly proportional to the carbon atom concentration present in the original sample. Thus, the flame ionization detector gives HC concentrations in terms of carbon atom concentration.

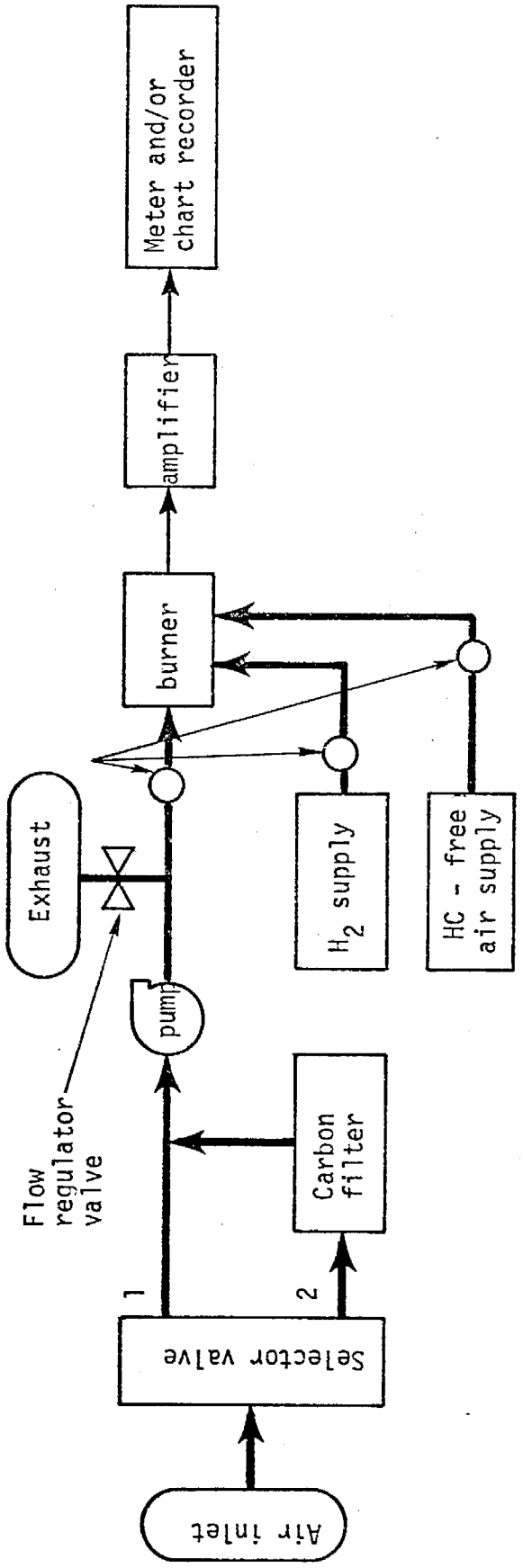
The advantages of flame ionization detection of hydrocarbons are: 1) water and other inorganic compounds cause very little interference with the measurements process; 2) virtually all hydrocarbons except formic acid can be detected; 3) the apparatus is considered inexpensive and reliable;[1] and 4) the apparatus is sensitive to small concentrations of hydrocarbons and gives linear response over a 10^6-fold range of carbon concentrations.[2] The most important disadvantage is the dependence of the reading on the flow rate of the sample; unless uniform flow is maintained, results are not reproducible. Another disadvantage is that the instrument's response to carbon atoms in small hydrocarbons is somewhat higher than that to large-molecule carbon atoms. Thus, instrument response to 2 ppm of C_{10} hydrocarbons will be lower than the response to 4 ppm of C_5 hydrocarbons, even though the carbon atom concentration is the same in both cases. While this doesn't necessarily affect the reproducibility of the results, it does cast doubt on the validity of the measurements, i.e., it indicates that the output

is directly proportional to the number of carbon atoms in the sample only if the relative concentrations of various hydrocarbon species are held constant.

One recent EPA-sponsored study concluded that the reproducibility of FID hydrocarbon readings is within $\pm$ 10%, while the absolute accuracy is about 85%.[1] FID instruments tend to work reasonably well, but do give occasional unaccountably poor readings.[1] Frequent recalibration of the instruments is critical, due to the span drift that can occur over periods of a few days.

Since flame ionization gives total hydrocarbon concentrations only, it is necessary to add other equipment to determine CH_4 and NMHC levels. The most commonly used modification is the addition of a gas chromatograph stripper column, which removes water, CO_2, and large hydrocarbons from the sample and which separates CH_4 from the other hydrocarbons in the sample (see Figure 4.1). The principle of operation is simple: hydrocarbons tend to move through the stripper column at rates inversely proportional to their boiling points.[3] Methane, being the lightest and most volatile hydrocarbon, travels through the silicon gel or other column packing material much faster than the heavier hydrocarbons and reaches the flame ionization detector first. The methane concentration can then be subtracted from the total hydrocarbon level to yield the NMHC concentration of the sample.

The primary disadvantage of the gas chromatographic technique is the high level of operator skill required and the relatively high complexity



Valve setting 1 = THC
2 = NMHC

Figure 4.1 Schematic Diagram of Hydrocarbon Analyzer System

and cost of the instrument. The analytical conditions must sometimes be readjusted repeatedly until good separation results are obtained,[3] and temperature control and calibration must be carefully watched.[4] The method is at best a semicontinuous one, since the CH_4 from the sample requires 2 to 4 minutes to travel through the glass separator column. However, at the present time, gas chromatography is the only commercially available method capable of reliably determining NMHC concentrations.

It is possible to measure CH_4 concentrations by FID without the use of a GC, by using a methane-saturated activated carbon column to absorb all NMHC from the sample gas. This technique, which is used by most stations within Los Angeles county, has two significant error sources associated with it. First, the activated carbon column absorbs certain hydrocarbons more completely than others. Second, the solvent used for the extraction of hydrocarbons from the column is itself a hydrocarbon, which can interfere with the FID readings.[3] The temperature of the absorber column must be rigidly controlled, since the methane saturation level of the activated carbon changes with temperature. Any change in temperature can therefore result in the absorption or release of CH_4 by the column, which could interfere with the FID reading. The service lifetime of the carbon in the column is short; it can be lengthened by the use of a larger column, but this slows the response time and gives higher temperature-induced errors in the readings.

The response of a flame ionization detector to a given sample of mixed hydrocarbons will be higher if the detector is used with a gas

chromatographic separator column. Thus, total hydrocarbon readings are actually somewhat lower than the actual ambient concentrations, and NMHC readings, as total hydrocarbons less methane, also tend to be low.[5]

The principal alternative to flame ionization detection, nondispersive infrared detection (NDIR) provides results which do not directly correlate with those of the FID. Infrared response of a carbon compound depends on its molecular geometry, rather than directly on its number of carbon atoms. Also, the method is highly sensitive to the interference of water vapor and relatively insensitive to several important air pollution hydrocarbons.

One source of error in FID or NDIR hydrocarbon measurement is the absorption of polar hydrocarbons from the sample gas into the surface of plastic sample bags. Glass, being relatively inert, is a good alternative to plastic; among plastics, Tedlar is a good choice.[3,4] Two other error sources in hydrocarbon measurement are leakage and contamination of the pump used in the sampling apparatus. These errors are avoided by the use of a vacuum pump downstream of the sampler, instead of a pressure pump upstream of it.[5,6]

One of the most critical studies of hydrocarbon measurement techniques was made by Scott Environmental Technology.[7] One of the major conclusions of this nationwide study was that "inaccuracies in current data make it impossible to determine whether ambient air quality is in compliance with the standards." Major error sources were found to be: 1) operator error (deviation from standard procedures); 2) contaminated span gases used in calibrations; 3) span gas diluted with gases other than air; 4) span gas improperly checked for methane; 5) contamination-caused zero errors; and 6) instrument zero and span drift. Sixteen different instruments from 5

different manufacturers were represented in this study, in which bottles containing known concentrations of several hydrocarbons were given to various monitoring agencies for analysis. The sample flow rate was found to be critical to hydrocarbon and NMHC measurements. The means and medians of the various test measurements corresponded well with the actual prepared concentrations, but the respective standard deviations of values were nearly 100% of the means. Zeroing errors abounded, with 7 of the 16 sampling stations recording hydrocarbon values of over .5 ppm for hydrocarbon-free gas. The study recommended that zeroing gas be used for instrument zeroing, in contrast to the manufacturer's instructions, which claim that the equpment's automatic zeroing and catalytic purifier permit zeroing with air.

Span errors of 10% were commonly encountered in the study, which implies that 10% measurement errors are not uncommon. Since total hydrocarbons and CH_4 are spanned separately, NMHC readings have especially high variability. For example, if a given CH_4 span is high and the corresponding total hydrocarbon span is low, the NMHC, which is the difference between them, will be far lower than it should be.

A major finding of the Scott labs study is that the percent measurement error at low hydrocarbon concentrations greatly exceeds that at high concentrations. For example, 50% of the sites tested reported high hydrocarbon levels within 10% of the correct values, but only 30% were within 20% of the correct low hydrocarbon levels.

The Scott report's major recommendation was that all hydrocarbon monitoring stations periodically be presented with known-concentration samples for analysis. The results of such a study could then be used in quality control.

The Scott report indicates that the HC data available are probably less accurate than Federal performance standards require. In contrast to the monitor performance noted above, the Federal Government's performance standards for NMHC monitors are:[8]

sensitivity threshold	.1 ppm
zero drift	.2 ppm
span drift	5%
lag time	10 min
noise	.05 ppm
maximum interference	.2 ppm (total interference)

Were these standards met, there would be little doubt about the adequacy of the data for the empirical study. However, the Scott study points out the need for a quality check of all HC data to be used in the empirical analysis. This is one subject of Chapters 5 and 6.

4.1.2 Oxides of Nitrogen, NO, and NO_2 Monitors

NO, NO_2, and NO_x measurement in the SCAB and SEDAB is almost universally by the modified Saltzman colorimetric technique. In this procedure, the air sample is mixed with the Saltzman reagent, which consists of sulfanilamide in acetic acid. The sulfanilamide, N-(1-napthyl)-ethylene-diamine dihdrochloride, reacts with the NO_2 present in the air sample to form a red azo dye, which absorbs light at approximately .55 μ wavelength.[5,9] Theoretically, the color intensity of the resultant dye is proportional to the original NO_2 concentration of the air sample. The .55 μ light absorbance of the solution is then measured on a colorimeter, whose meter reading is proportional to the logarithm of the dye concentration, and therefore proportional to the logarithm of the NO_2 concentration of the air as well.

The Saltzman technique measures only NO_2 levels, but can be modified to measure NO and NO_x as well. Two Saltzman technique modifications are prevalent in the SCAB and SEDAB. In the first, the sample air flow is split and introduced into two Saltzman mixing chambers. The air is fed directly into one chamber, where the NO_2 concentration of the sample is determined. The air going to the second chamber is first passed through an acid potassium permanganate bubbler, which converts the NO in the air to NO_2, whose concentration is then measured in the second mixing chamber. Assuming that all of the NO is converted to NO_2, the reading in the second chamber is the NO_x level (NO + NO_2) of the ambient air, while the reading in the first chamber is the NO_2 level (see Figure 4.2). In the second, the sample air flow passes through one chamber, where the NO_2 level is measured in the usual manner. Next, the air leaves this chamber and passes through an acid potassium permanganate bubbler where the NO is converted to NO_2. The air then enters the detector, where the NO_2 concentration, which is theoretically equal to the original NO concentration, is measured (see Figure 4.3). NO_x is then the sum of the NO and NO_2 readings. It should be noted that the use of this method assumes that all of the NO_2 originally present in the air is consumed by the reagent in the first chamber, and that all of the NO is converted to NO_2 before the sample is introduced to the second chamber. In practice, the NO-to-NO_2 conversion efficiency is about 95%.[10]

Two calibration techniques, static and dynamic, are used with colorimetric NO_2 analyzers. In the static method, sodium nitrite is mixed with the Saltzman reagent to produce the dye, and the relationship between sodium nitrite concentration and color intensity is noted. The major

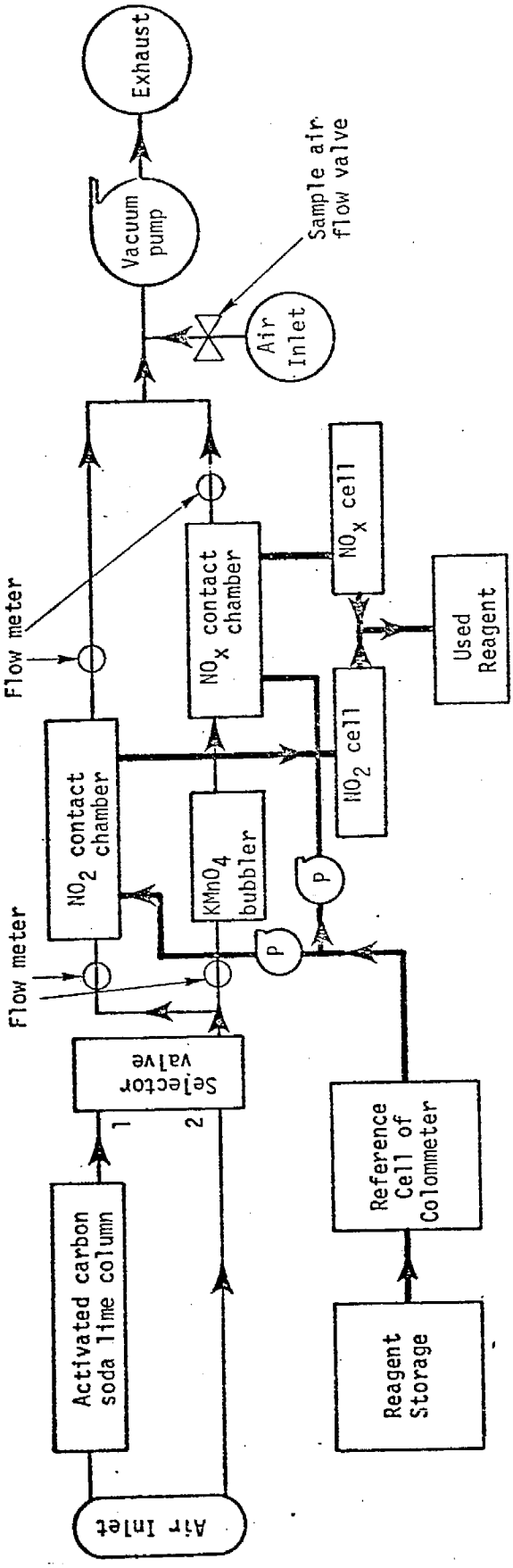


Figure 4.2 Schematic Diagram: NO_2, NO_x Analyzer

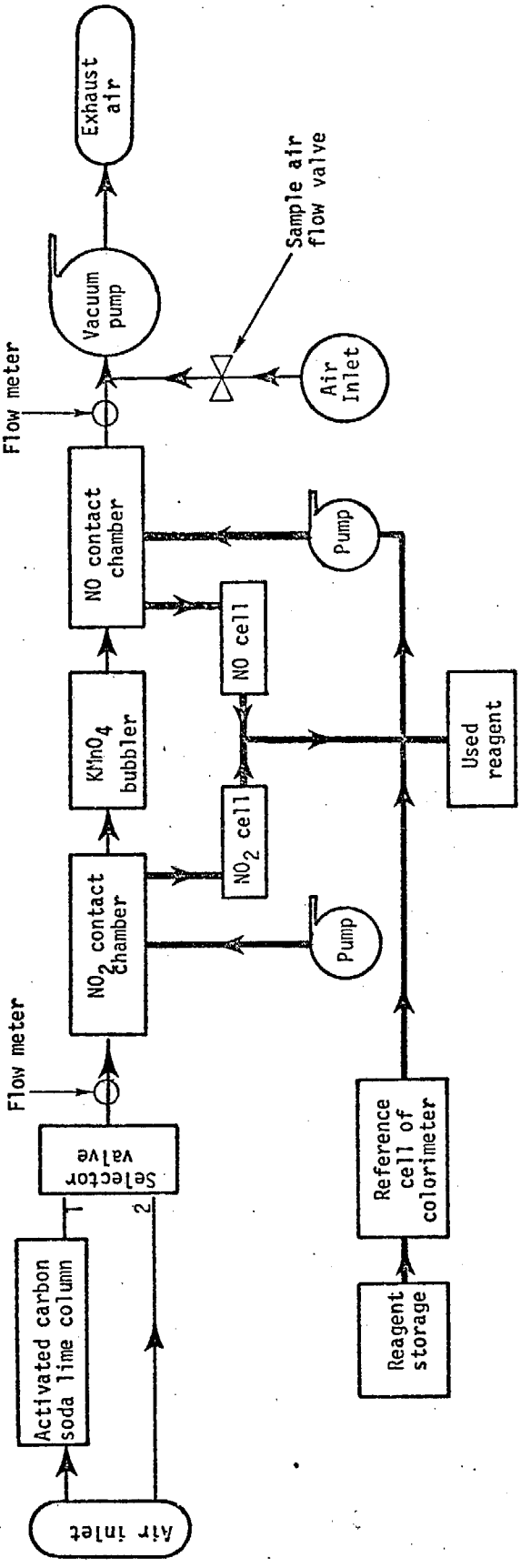


Figure 4.3 Schematic Diagram: NO, NO_2 Analyzer System

difficulty with this technique is that it cannot be directly related to the measurement of airborne NO_2, because the reaction efficiencies of NO_2 gas and sodium nitrite NO_2 differ. Virtually all of the NO_2 in $NaNO_2$ reacts with the Saltzman reagent to form the dye, but only approximately 72% of the NO_2 gas in the sample reacts in this manner.[10] If this "Saltzman factor" of 72% were universal among Saltzman instruments, there would be no problem. However, every instrument has its own Saltzman factor, which can be anything from 70% to 90%.[10] If static calibration is used, instruments with different Saltzman factors will give different results. Fortunately, a given instrument's Saltzman factor is consistent over time. Therefore, as long as an instrument is kept in calibration by the static method, all readings taken by it should be consistent with one another.

A better, much more expensive calibration method is dynamic calibration with a gas sample containing known concentrations of NO_2 and NO. This form of calibration tests the entire sampling system, not just the colorimeter, and does not require a Saltzman factor correction.

Because instrument calibration is heavily dependent on the flow rates of the sample gas and the reagent, it is essential that the instrument operator regulate flow rates critically. Another potential error source is the absorption of color by substances other than the NO_2-generated azo dye, causing excessively high concentration readings. Conversely, the NO_2 readings obtained in particulate-laden air can be somewhat low because NO_2 tends to adhere to particulates, which are removed by the sampler's filter. The adherence of NO to particulates is not believed to be significant.[11]

The accuracy of the Saltzman technique is normally about $\pm$ 3%,[11] but a few minor chemical interferences are documented or suspected. The most serious of these is SO_2 interference. For example, 15 ppm SO_2 can cause an 8% drop in a 100 ppm NO_2 level. Another error source is absorption or desorption of NO_2 on the walls of the tank in which the sample is collected. To reduce this error, a flow system should be preconditioned for a few weeks prior to use. One can do this by exposing the system to NO_2 concentrations comparable to the ambient levels. Ozone can also introduce some error in NO_2 measurements.[9] Daily zeroing and weekly recalibration of the instruments is recommended, as is frequent cleaning to remove solid deposits which can cause air flow obstruction.[9] Since Saltzman factor of any given instrument varies less than .05 over time,[10] static recalibration is probably sufficient, as long as the initial calibration is dynamic.

4.1.3 Oxidant/Ozone Monitors

Strongly oxidizing compounds present in the air embrittle rubber, cause eye and respiratory irritation, and are believed to be detrimental to health. Chief among the oxidants is ozone, O_3. Oxidant (OX) data analysis is complicated by the fact that some stations measure O_3 concentration, while others measure OX. As this section will demonstrate, O_3 and OX readings, while usually similar for a given sample of air, are not strictly equivalent. Thus, before the empirical analysis, total oxidant readings will be converted to approximate equivalent ozone concentrations using a formula presented below.

In the SCAB and SEDAB, total OX measurement is made using the potassium iodide (KI) method, in which the oxidizing agents in the air interact with

the KI to release free iodine, i.e., the iodine is oxidized from its colorless ionic form in the KI solution, I-, to the neutral form, I_2. Since the I_2 is strongly colored and the amount of I_2 released is proportional to the net oxidizing strength of the original air sample, the OX concentration of the ambient air can be determined from the degree of color (light absorbance) of the KI solution.

Strongly oxidizing compounds, like O_3, promote the release of free iodine from KI, while reducing compounds, such as SO_2, inhibit this reaction. The net KI to I_2 reaction depends primarily on the relative concentrations of O_3, NO_2, and SO_2 because other strong oxidizing and reducing compounds occur at far lower concentrations in the ambient air. Because of this, one can estimate the O_3 concentration present in the air from the oxidant, NO_2, and SO_2 levels. The empirically verified correction equation is: ozone = oxidant - $.2(NO_2)$ + SO_2, where oxidant, NO_2, and SO_2 are the respective measured levels of these pollutants in ppm or other molar concentration units.[12] The coefficient of the NO_2 concentration is somewhat sensitive to the strength of KI solution used in the analytical process; .2 is appropriate for 10% KI soluation, while .3 should be used for 20% KI. In the empirical analysis, the above expression will be used to change all OX data into equivalent O_3 estimates, while O_3 readings will be left unchanged. (Some monitoring stations outside of SCAB and SEDAB use CrO_3 scrubbers to remove SO_2 from the sample air. While this does eliminate the SO_2 interference in oxidant readings, it also converts NO to NO_2, thereby introducing NO interference. Since the Los Angeles area stations do not use scrubbers, NO correction is inappropriate.)

Although the California Air Resources Board and the Los Angeles APCD use the same total oxidant measurement techniques, they calibrate their instruments by different methods. The APCD calibrates its ozone generator with an unbuffered 2% KI solution.[13] Then the ozone generator is used to create an oxidant sample of known concentration, which is used to calibrate the OX meter. In contrast, the ARB used neutral buffered KI (NBKI) to calibrate the ozonator. Although this calibration procedure is more precise, or repeatable, than the APCD method, it is also apparently less accurate, i.e., instruments calibrated by the ARB method consistently read high by 20%. To resolve this inconsistency in the SCAB oxidant data base, the ARB took the following steps:

1) All oxidant data other than that collected by LA APCD were multiplied by an .8 correction factor, to bring them into approximate conformity with the LA APCD results;

2) by June, 1975, all non-Los Angeles stations were required to convert from NBKI calibration to calibration by portable UV photometer (e.g., the Dasibi instrument).

Stations using chemiluminescent or UV ozone monitors but calibrating their ozone generators by NBKI have likewise switched to UV calibration. For example, the stations of the San Bernardino APCD use gas phase chemiluminescent ozone photometers, which measure the light given off by the reaction of ozone with ethylene. This detection method is believed to be ozone-specific and reasonably accurate. The data obtained by this method

should be comparable to the Los Angeles APCD oxidant data, if the latter are corrected for NO_2 and SO_2 interference. Chemiluminescent monitors are calibrated using ozone generators, which in turn were formerly calibrated by the NBKI method. Since June 1975, these ozone generators have been calibrated by UV photometry, and the ARB has multiplied all earlier ozone data by .8 to compensate for the former NBKI calibration.

With the appropriate correction factors applied, SCAB and SEDAB oxidant/ozone data are probably reasonably accurate and internally consistent. There is no reason to believe that O_3/OX measurement accuracy will seriously interfere with the proposed statistical analysis.

4.2 SPECIFIC PRACTICES OF THE MONITORING AGENCIES

As the preceding discussion indicates, the accuracy of the ambient air measurements made by a given agency depends heavily upon the measurement procedures it follows. Fortunately, the SCAB APCD's are among the most experienced and conscientious in the nation, as is evidenced by their relatively high scores in earlier data quality tests.[14] The SCAPCD's monitoring procedures will be discussed in this section, while the statistically estimated accuracy of their measurements is the subject of Chapters 5 and 6.

NO_x, NO, and NO_2 measurement in the SCAB, as previously noted, is by the Saltzman colorimetric method. The major difference among agencies is that Los Angeles and Riverside counties measure NO and NO_2 concentrations, adding these to determine NO_x, while Orange and San Bernardino counties measure NO_2 and NO_2, reporting the difference as NO. The latter

method may be slightly preferable for the present study, in which NO_x and NO_2 are of greatest interest. However, since $NO/NO_2/NO_x$ measurements are generally within 10% of the true values, this is not believed to be a serious limitation.

Several different oxidant/ozone measurement techniques are used in the SCAB. The reproducibility of data from stations using UV photometric calibration is higher than that from stations using unbuffered KI calibration (e.g., the Los Angeles APCD).[15] However, as Chapter 6 indicates, the oxidant data among SCAB monitoring sites correlate well.

The greatest inter-site measurement disparities are expected to be among hydrocarbon monitors, particularly among NMHC monitors. Two sites use gas chromatographic separation of hydrocarbons, while the others use the methane-saturated activated carbon filter for methane isolation. The gas chromatograph flame ionization detector (GC/FID) is potentially a more accurate device than the activated carbon flame ionization detector, but is significantly more difficult to use properly. Since gas chromatograph results are highly sensitive to the manner in which the instrument is operated, and since the activated carbon columns give rise to very temperature-sensitive readings, THC data rather than NMHC data may be used in the empirical analysis, in spite of the fact that NMHC is a better representation of the smog-forming potential of the air than is THC. FID, the HC measurement method used by all SCAB sites, is capable of providing very reproducible results as long as basic calibration and operation methods are observed. Because FID is a relatively simple technique, it

should be less sensitive to procedural variations than some of the other monitoring methods.

4.3 POTENTIAL PROBLEMS IN THE COLLECTION OF METEOROLOGICAL DATA

It is anticipated that the air quality data will provide more error sources and potential problems than will the meteorological data, since the latter generally are obtained from simpler, more reliable instruments. However, there are a few potential problems involved in the collection and use of meteorological data, and these are the subject of this section.

Because of the documented unreliability of the Los Angeles and Riverside County instruments,[16] it is probable that relative humidity data should not be used in the empirical modeling. Humidity does affect the rates of formation and decay of several pollutants and would therefore normally be included in the study. In this case, however, it seems preferable to omit the humidity data rather than to introduce an unknown error by using it.

Solar radiation data are available only into 1974, and for only two sites, Los Angeles Airport, and downtown Los Angeles. The intensity of solar radiation is correlated with the rates of the various photochemical reactions that convert raw exhaust to photochemical oxidants and would therefore normally be included in the empirical analysis. However, 1974 and 1975, the years for which the most complete air quality data are available, are also the years for which solar radiation data are unavailable. Thus, solar radiation may be omitted from some parts of the study.

Wind speed and direction data are widely available throughout the SCAB and SEDAB, particularly within Los Angeles County. The major caveat to the

user of these data is that within the SEDAB and SCAB at least three different systems of measuring wind velocity are used. The three main systems are: 1) The average wind speed and direction is taken for two minutes each hour; then the average wind velocity between 2:59 and 3:01, for example, is reported as the hourly wind speed for 3:00. 2) The average wind speed and direction is taken from 30 minutes before the hour to thirty minutes after the hour. This is a true hourly average wind velocity, unlike the above 2-minute average. Under this system, the 3:00 hourly average wind velocity is the average of all data from 2:30 to 3:30. 3) At Los Angeles APCD headquarters in downtown Los Angeles, a third system is used for historical reasons. Under this system, the hourly average wind direction is the most frequently occurring wind direction during the given hour, while the hourly average wind speed is the total number of miles of wind passing through the station during that hour. This would be nearly consistent with 2) above, except that the reported 3:00 wind speed is actually the average wind speed for the interval 3:00 to 4:00.

In order to minimize errors introduced by the problems mentioned above, the empirical modeling study will use the reported wind speed and direction for all stations except downtown Los Angeles. At downtown Los Angeles, the 3:00 average wind speed will be computed as the average of the 2:00 and 3:00 reported values, which is actually the 2-hour average from 2:00 to 4:00. Except on days with either gusty or extremely light winds, wind speed and direction change only slowly during the day. Therefore, the mixing of hourly average and two-minute average wind data should introduce

no major errors, although ideally only the true hourly averages should be used. SCAB area stations reporting true hourly average wind data are indicated by an asterisk in Table 2.9. Those without an asterisk use the 2-minute average. As new monitors are established, these are almost exclusively of the automatic recording type and are set up for hourly average recording.

Hourly temperature data are instantaneous once-per-hour readings which are presumed to reflect the respective hourly average temperatures at each site. Since temperatures generally fluctuate slowly during the day and since photochemical smog reactions are not highly sensitive to slight temperature variations, the use of instantaneous instead of true hourly average values should represent only a minor error source.

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5.0 DATA VERIFICATION AGAINST SPECIAL MONITORING PROJECTS

The most direct way of assessing the quality of routine air monitoring data is to compare the routine data to measurements made at the same locations during special monitoring projects. The Air Resources Board Mobile Air Quality Monitoring Program (Mobile Van Program) provides some data sets that are ideal for this comparison. One of the purposes of the Mobile Van Program is to "conduct parallel monitoring adjacent to fixed stations to ensure comparability of measurements."[1] In addition to the mobile van program, the ARB El Monte Laboratory has performed a series of special hydrocarbon field tests. This chapter will use the data from these ARB programs to investigate the quality of routine monitoring data.

5.1 ARB MOBILE VAN PROGRAM

As part of the Mobile Air Quality Montoring Program, the ARB put into service four mobile monitoring vans in 1973.[1] These vans are equipped with the latest generation of monitoring equipment to measure eight pollutant variables as well as wind speed, wind direction, and temperature. One of the purposes of the Mobile Van Program is to assist in the ARB's Air Monitoring Quality Assurance Program. Accordingly, the mobile vans have been used to conduct parallel measurements adjacent to fixed monitoring stations.

To date, the ARB staff has conducted statistical analyses of parallel monitoring data for seven sites* in the SCAB and one site** in the SEDAB.[2]

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*Azusa, Downtown L.A., Pasadena, Pomona, Anaheim, La Habra, and Rubidoux.

**Banning

All of these statistical analyses involve field tests performed in 1975. The ARB analyses, based on daily maximum one-hour concentrations, include correlation coefficients, regression coefficients, and ratios of means. Tables 5.1 and 5.2 summarize the correlation coefficients and ratios of means for the three pollutants of interest in the present study: oxidant/ozone, total nitrogen oxides, and hydrocarbons. For comparison purposes, results are also included for nitrogen dioxide and carbon monoxide.

As indicated at the top of Tables 5.1 and 5.2, the ARB monitoring methods are different than the APCD monitoring methods for each of the five pollutants (see Chapter 4 for a discussion of methods). The ARB vans are equipped with relatively new instruments, while most APCD stations have retained older techniques in order to maintain continuity in the data record. Thus, a complete correspondence cannot be expected between the ARB and APCD data sets.

Since the empirical modeling study will be based on daily fluctuations of oxidant and precursors, the data quality statistic of most interest is the correlation coefficient (R) which indicates the agreement between relative variations in measured concentrations. Table 5.1 demonstrates that the oxidant/ozone data appear to be of especially high quality with respect to relative variations. Six of the eight oxidant/ozone tests yield correlations of .96 or higher. The high correlations for oxidant/ozone are due to the precision of the monitoring techniques (see Chapter 4) as well as to the relative insensitivity of a secondary pollutant to monitor location (see Table 5.3 for the distances between each pair of probes).

The correlations between the ARB and APCD NO_x measurements are good, though not as high as the oxidant/ozone correlations. The NO_x correlations

Table 5.1 Correlation Coefficients for Daily Maxima in ARB Mobile Van Tests[2]

STATIONS AND DATES	OXIDANT/OZONE APCD KI Oxidant Vs. ARB UV Phot. O_3	NITROGEN OXIDES APCD Color. NO_x Vs. ARB Chem. NO_x	TOTAL HYDROCARBONS APCD FI THC Vs. ARB GC/FI THC	NITROGEN DIOXIDE APCD Color. NO_2 Vs. ARB Chem. NO_2	CARBON MONOXIDE APCD NDIR CO Vs. ARB GC/FI CO
LOS ANGELES COUNTY					
Azusa (7/9/75-8/12/75)	.97	.97	.90	.86	.55
Downtown L.A. (10/8/75-11/18/75)	.90	.97	.93	.96	.96
Pasadena (6/17/75-7/9/75)	.98	.86	.47	.96	.74
Pomona (7/10/75-8/12/75)	.97	.79	.77	.91	.83
ORANGE COUNTY					
Anaheim (8/8/75-9/16/75)	.91	.92	.56	.78	.75
La Habra (8/5/75-9/18/75)	.97	.76	--	.88	--
RIVERSIDE COUNTY					
Rubidoux (10/1/75-11/19/75)	.97	.90	.71	.96	.87
Banning (10/13/75-11/19/75)	.96*	--	.51	--	.83
AVERAGE CORRELATION COEFFICIENT AMONG STATIONS	.95	.88	.69	.90	.79

*The APCD site at Banning measures O_3 by UV photometry.

Table 5.2 Ratios of Mean APCD Concentrations to Mean ARB Concentrations[2]

STATIONS AND DATES	OXIDANT/OZONE APCD KI Oxidant ÷ ARB UV Phot. O_3	NITROGEN OXIDES APCD Color. NO_x ÷ ARB Chem. NO_x	TOTAL HYDROCARBONS APCD FI THC ÷ ARB GC/FI THC	NITROGEN DIOXIDE APCD Color. NO_2 ÷ ARB Chem. NO_2	CARBON MONOXIDE APCD NDIR CO ÷ ARB GC/FI CO
LOS ANGELES COUNTY					
Azusa (7/9/75-8/12/75)	.84 ± .02*	1.16 ± .04	.84 ± .05	1.05 ± .07	1.47 ± .16
Downtown L.A. (10/8/75-11/18/75)	1.10 ± .06	.68 ± .02	.83 ± .03	.64 ± .03	1.24 ± .05
Pasadena (6/17/75-7/9/75)	.95 ± .03	.92 ± .05	.76 ± .08	1.04 ± .03	1.86 ± .19
Pomona (7/10/75-8/12/75)	.83 ± .02	1.10 ± .09	.99 ± .03	.90 ± .04	1.20 ± .08
ORANGE COUNTY					
Anaheim (8/8/75-9/16/75)	.65 ± .05	.82 ± .05	.71 ± .05	.89 ± .07	1.30 ± .07
La Habra (8/5/75-9/18/75)	.85 ± .03	.62 ± .04	--	.79 ± .03	--
RIVERSIDE COUNTY					
Rubidoux (10/1/75-11/19/75)	.95 ± .03	.74 ± .04	1.17 ± .09	.56 ± .02	1.03 ± .07
Banning (10/13/75-11/19/75)	.98 ± .04	--	1.29 ± .17	--	1.11 ± .10
AVERAGE RATIO AMONG STATIONS	.89	.85	.94	.84	1.32

*95% confidence limits

Table 5.3 Distances Between Corresponding APCD and ARB Monitoring Probes[2]

STATIONS AND DATES	PROBE HEIGHTS		APPROXIMATE HORIZONTAL DISTANCE BETWEEN PROBES
	APCD	ARB	
LOS ANGELES COUNTY			
Azusa (7/9/75-8/12/75)	8 ft.	30 ft.	25 ft.
Downtown L.A. (10/8/75-11/18/75)	75 ft.	100 ft.	90 ft.
Pasadena (6/17/75-7/9/75)	18 ft.	30 ft.	1.2 miles
Pomona (7/10/75-8/12/75)	21 ft.	30 ft.	0.5 miles
ORANGE COUNTY			
Anaheim (8/8/75-9/16/75)	15 ft.	30 ft.	25 ft.
La Habra (8/5/75-9/18/75)	15 ft.	30 ft.	1000 ft.
RIVERSIDE COUNTY			
Rubidoux (10/1/75-11/19/75)	20 ft.	30 ft.	50 ft.
Banning (10/13/75-11/19/75)	30 ft.	30 ft.	25 ft.

in Table 5.1 range from .79 to .97 and average .88 among the sites. The lower correlations for NO_x compared to oxidant may be due to any of three factors: (1) lesser precision in the NO_x monitoring methods, (2) interference of SO_2 with the colorimetric NO_x method, and (3) sensitivity of a primary pollutant measurement to probe location. The last of these three factors may play an especially important role in the low correlations at Pomona and La Habra, .79 and .76, respectively. Table 5.3 indicates that the distances between probes are quite high in these two cases. If the low correlations for Pomona and La Habra could indeed be attributed to probe location, then the quality of the NO_x monitors might be nearly as high as for the oxidant/ozone monitors.

Out of all five pollutants listed in Table 5.1, the lowest correlation occurs in the case of hydrocarbons. Although Downtown L.A. and Azusa yield THC correlations of .93 and .90, all of the other sites produce correlations less than .80. The average correlation among the sites is only .69. As noted in Chapter 4, doubts have been raised with respect to the precision of hydrocarbon measurements; the low correlations probably reflect poorer data quality for hydrocarbons than for the other pollutants. Some of the discrepancies may also be due to probe location, particularly in the case of Pasadena ($R = .47$), where the probes were separated by 1.2 miles. Since hydrocarbons are primary pollutants, hydrocarbon concentrations are expected to be sensitive to monitor position.

To provide the reader with a feeling for the data scatter associated with various degrees of correlation, Figures 5.1 to 5.3 present examples of scatterplots prepared by the ARB staff. These examples illustrate the amount of data scatter for correlations of .97, .86, and .76, respectively. Examples of lower correlations can be found in Section 5.2.

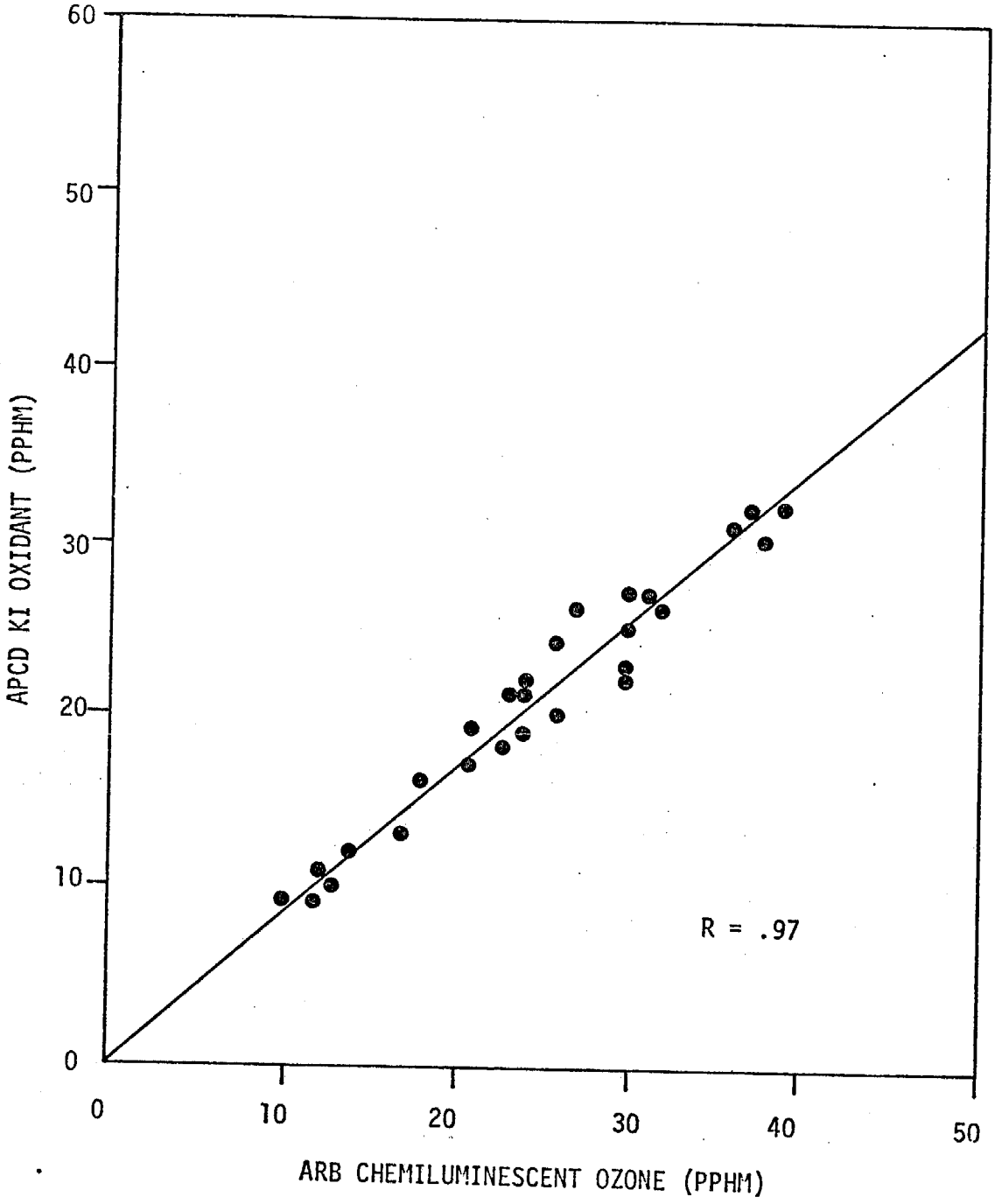


Figure 5.1. Example of Data Scatter for a Correlation of .97, Azusa Oxidant/Ozone Test, 1975

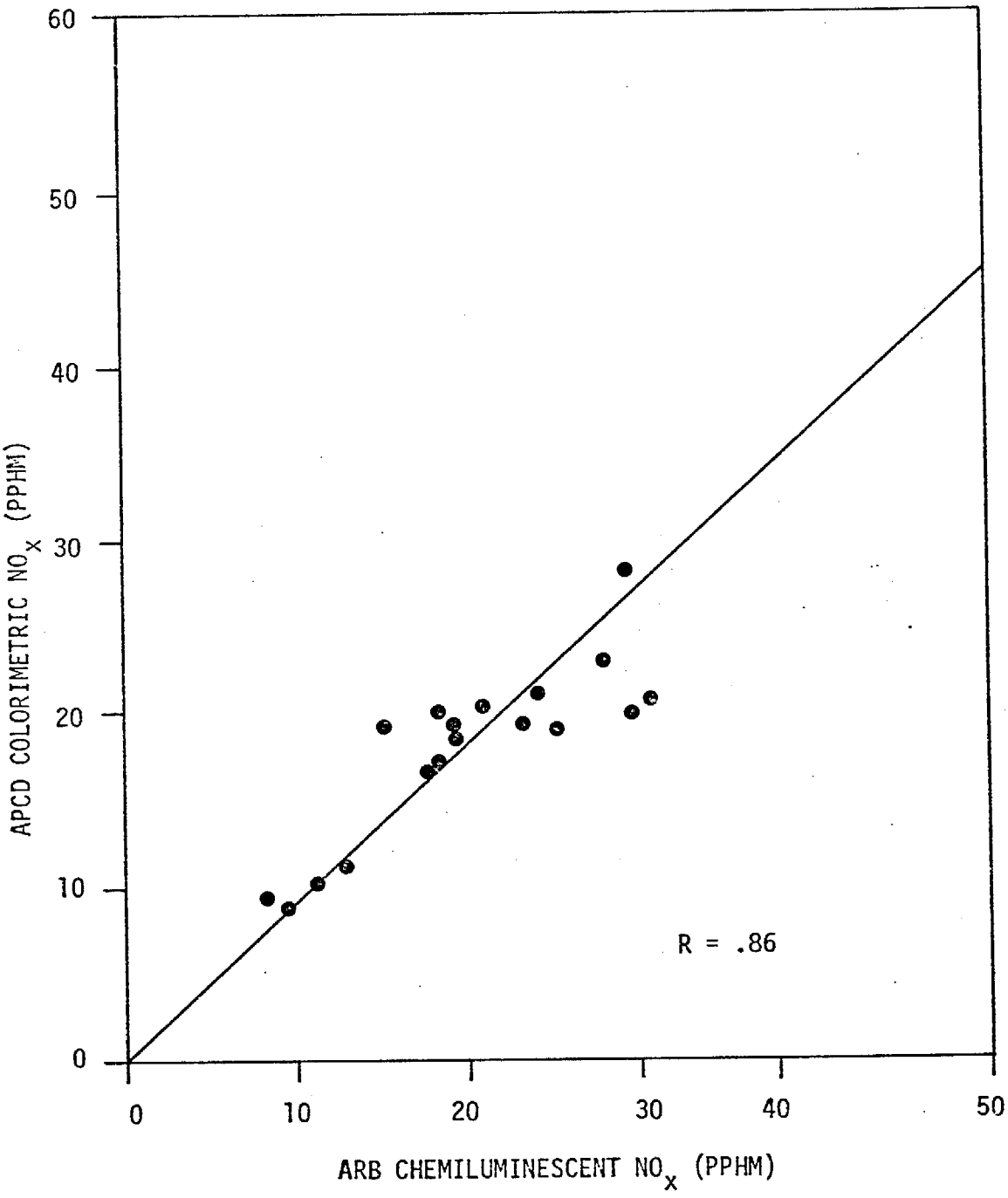


Figure 5.2. Example of Data Scatter for a Correlation of .86, Pasadena NO_X Test, 1975

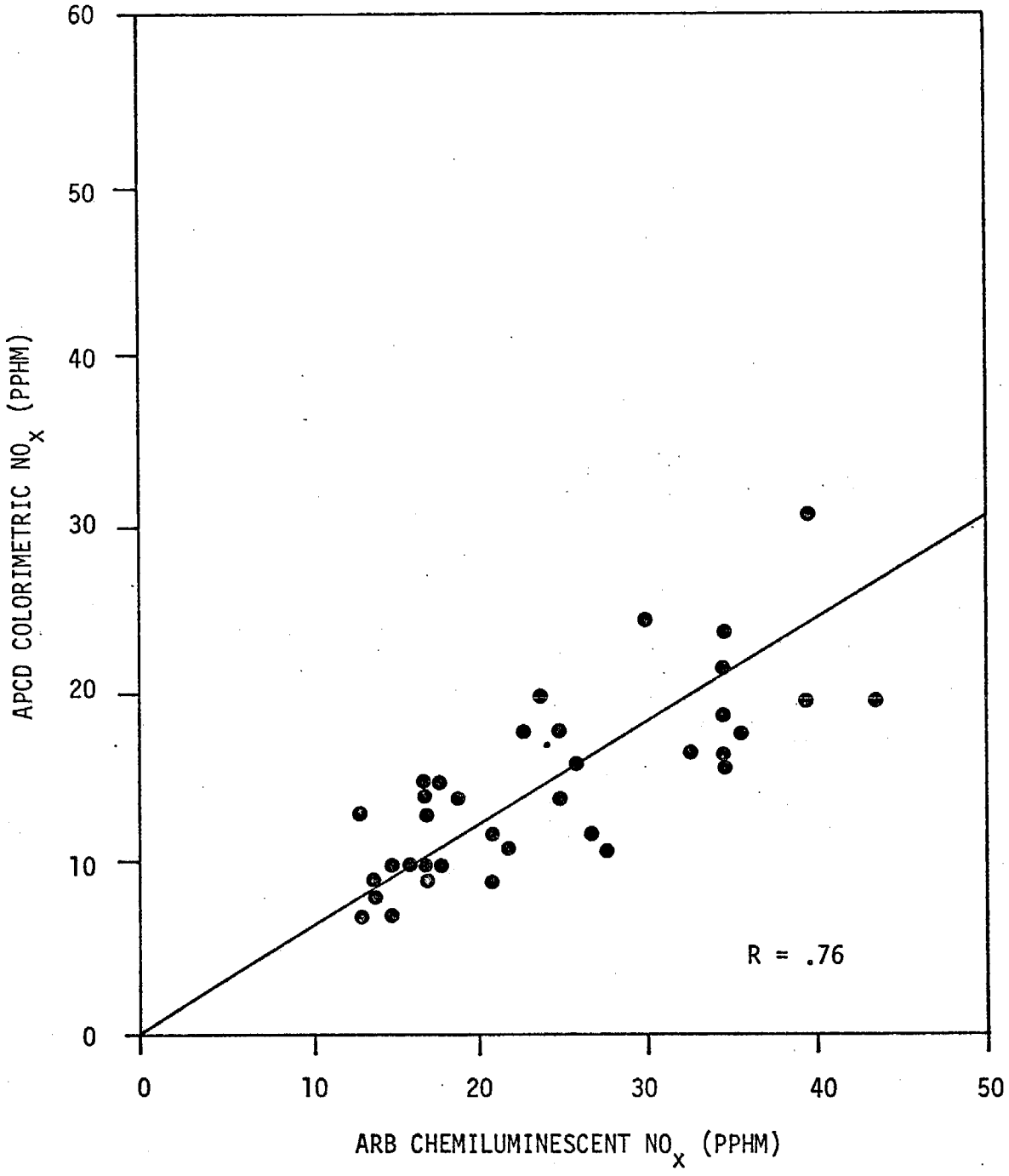


Figure 5.3. Example of Data Scatter for a Correlation of .76, La Habra NO_X Test, 1975

Table 5.2 summarizes the absolute agreement between the APCD and ARB measurements with respect to average pollutant levels. Although absolute accuracy is not as important as relative accuracy (i.e., precision in recording fluctuations) in the empirical modeling analysis, Table 5.2 deserves some discussion. Table 5.2 indicates that the APCD KI oxidant readings tend to be lower, on the average, than the ARB UV photometry ozone readings. Much of this discrepancy may be due to the negative SO_2 interference (see Chapter 4). The KI oxidant data used in the empirical modeling study will be corrected for SO_2 and NO_2 interference. The APCD colorimetric NO_x (and NO_2) measurements tend to be lower than the ARB chemiluminescent measurements. A negative SO_2 interference may be a partial cause for the differences in the NO_x (and NO_2) recordings. It is notable that the Los Angeles and Orange County APCD hydrocarbon data are lower than the ARB measurements, while the Riverside APCD hydrocarbon data are higher than the ARB measurements. The differences might be attributable to instrument calibration.

5.2 ARB HYDROCARBON FIELD EXPERIMENTS

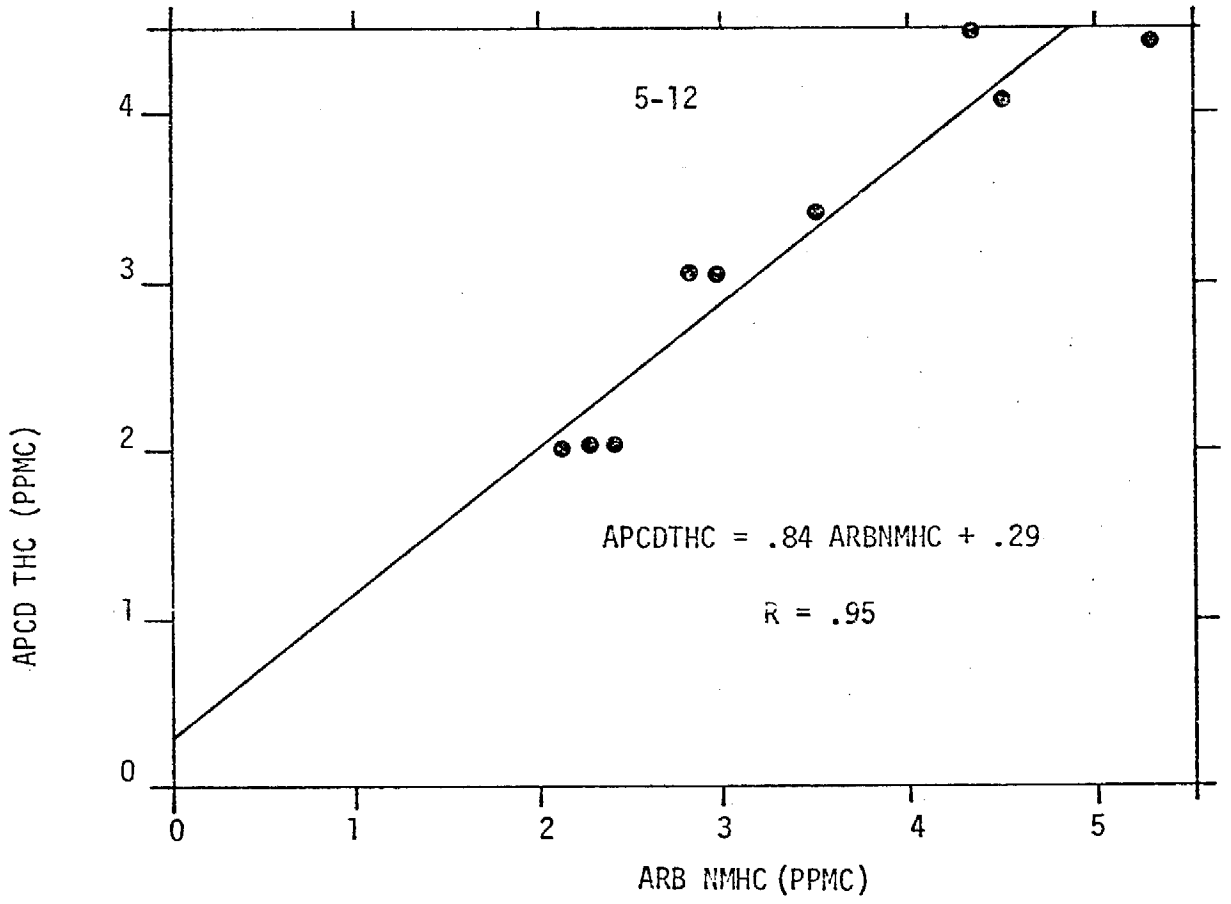
Because of questions raised in Chapter 4 and Section 5.1 concerning the quality of hydrocarbon measurements, it is desirable to conduct further checks on the hydrocarbon data. Hydrocarbon field experiments performed by the Air Resources Board supply data for these additional quality checks. During several months of each year since 1966, the Air Resources Board El Monte Laboratory has conducted hydrocarbon field tests at various locations in the South Coast Air Basin. The purpose of the ARB experiments is to provide information on ambient hydrocarbon composition, data on ambient hydrocarbon

trends, information on the spatial distribution of hydrocarbons, and data for source reconciliation studies.[3,4,5,6,7,8,9] Some of these field tests are conducted adjacent to existing APCD monitoring stations. This section uses ARB field data taken in 1971 and 1974 to conduct data quality checks for two APCD monitoring sites.

The ARB hydrocarbon field experiments of 1971 and 1974 involved daily measurements at several locations in the SCAB.[3,7] Two of these locations, Downtown Los Angeles and Azusa, were adjacent to APCD monitoring stations. The 1971 tests included measurements from 8:00-10:00 A.M. (PDT), while the 1974 tests included measurements from 6:00-9:00 A.M. (PDT). In order to conduct a data quality analysis for APCD recordings, corresponding measurements were retrieved from APCD tapes presently in TSC's data base.

The 1974 ARB experiments involved nonmethane hydrocarbons through C_{10}. Since these measurements typically represent only about 85% of all NMHC,[10] they will be denoted by NMHC'. As a check on the APCD data, the APCD THC and NMHC recordings were plotted against the ARB NMHC' recordings, and simple linear correlation/regression analyses were performed. The results are presented in Figures 5.4 and 5.5 and are summarized in Table 5.4. Two main conclusions stand out: (1) the 1974 Downtown Los Angeles data (R = .95 and .81) are of much better quality than the Azusa data (R = .68 and .49),* and (2) APCD THC measurements (R = .95 and .68) are more indicative of NMHC' variations than are APCD NMHC measurements (R = .81 and .49).

*Note that the Mobile Van Tests (Table 5.1) indicated that Downtown Los Angeles was slightly better than Azusa in 1975.



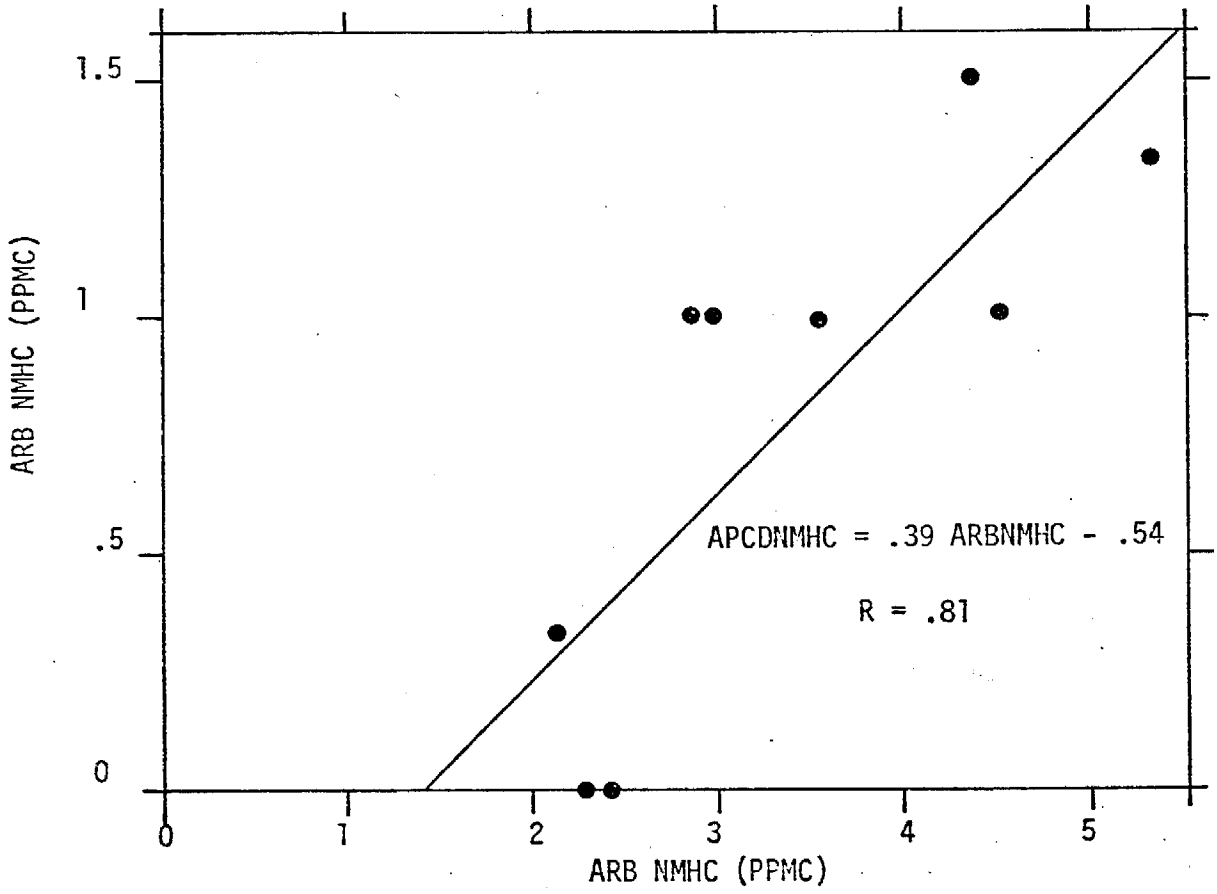
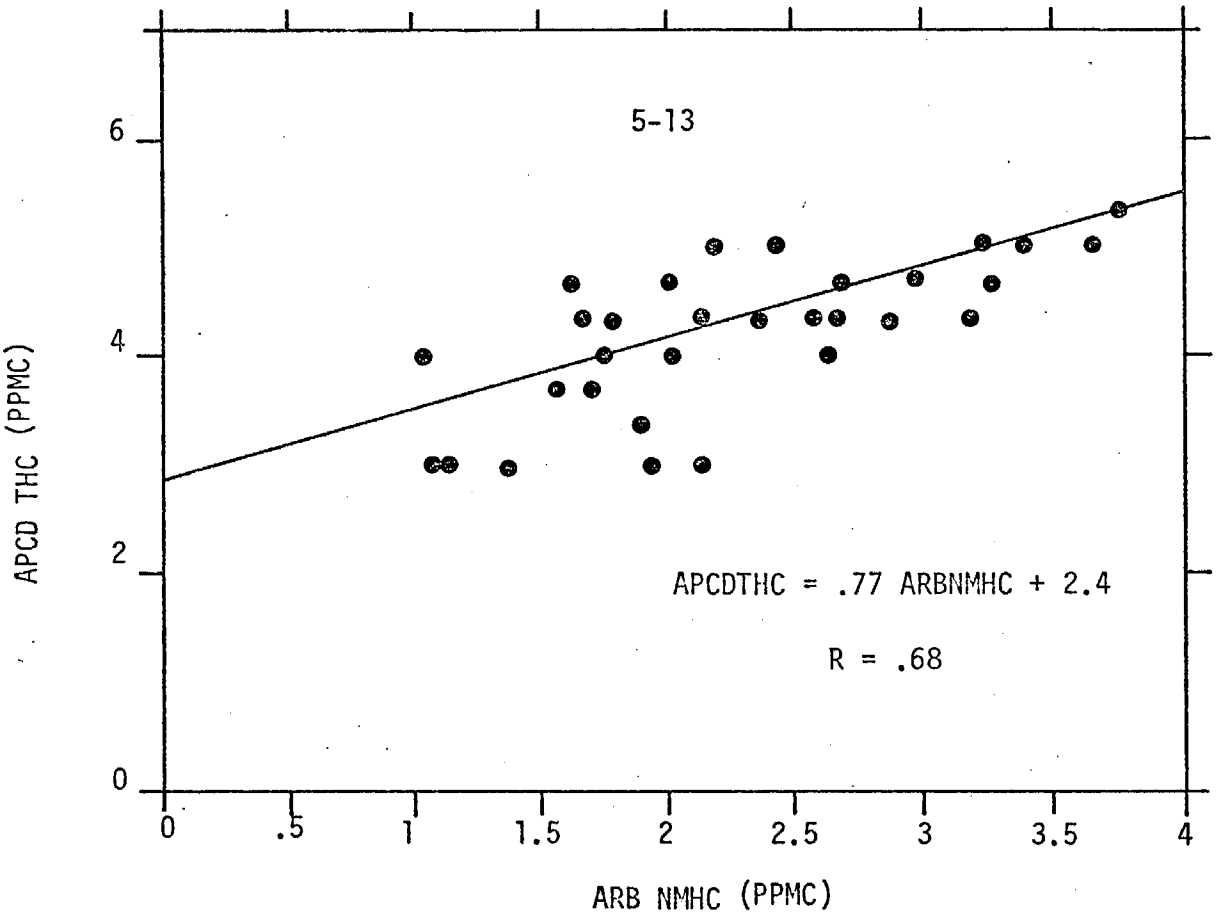


Figure 5.4 Comparison of APCD Hydrocarbon Data to ARB Field Test Data, Downtown Los Angeles, June 20-July 17, 1974.



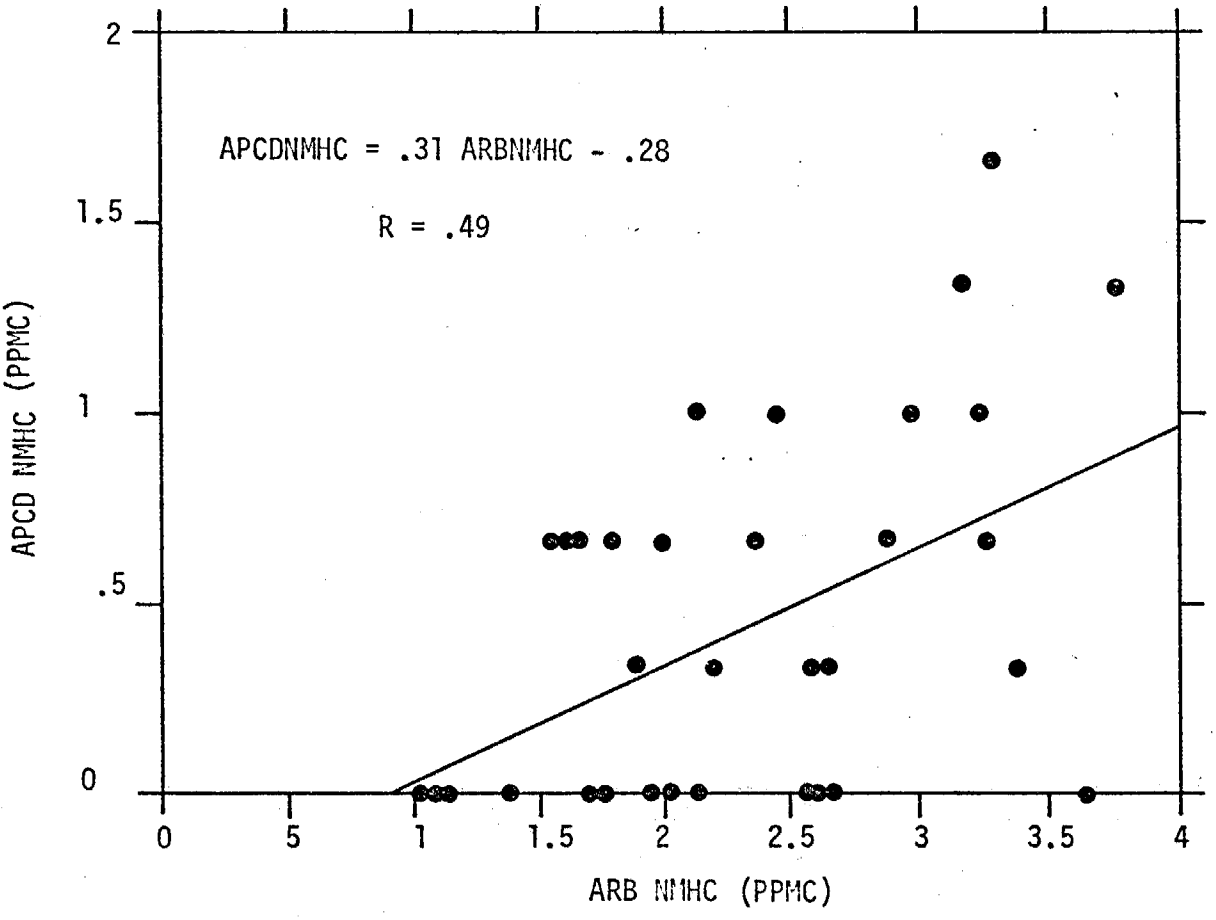


Figure 5.5 Comparison of APCD Hydrocarbon Data to ARB Field Test Data, Azusa, June 17-Sept. 5, 1974

Table 5.4 Correlation Coefficients of APCD Hydrocarbon Data with ARB Field Data, 1974

	APCD THC	APCD NMHC
Downtown Los Angeles ARB NMHC'	.95	.81
Azusa ARB NMHC'	.68	.49

The 1971 ARB field tests measured methane and nonmethane hydrocarbons (through C_{11}). As in the case of the 1974 tests, the ARB nonmethane hydrocarbon readings represent only about 85% of all NMHC.[10] Thus, they will be denoted by NMHC'. THC' will be defined as methane plus NMHC'. In the data quality check, APCD THC recordings were compared to THC' and NMHC', while APCD NMHC recordings were compared to NMHC'. Figures 5.6 and 5.7 present the results, while Table 5.5 summarizes the correlation coefficients. In 1971, the APCD Azusa data are about the same quality as the Downtown Los Angeles data. The THC measurements are of better quality than the NMHC measurements, and THC data give about as good a measure of NMHC' fluctuations as do NMHC data.

The conclusion that the APCD THC data are of better quality than the APCD nonmethane data is not surprising. NMHC recordings are obtained by subtracting methane (CH_4) measurements from THC measurements. Since both the CH_4 and THC data may have low precision, NMHC values, obtained by subtracting one uncertain measurement from another, are especially suspect. The uncertainties in the APCD NMHC data are compounded by high round-off error.

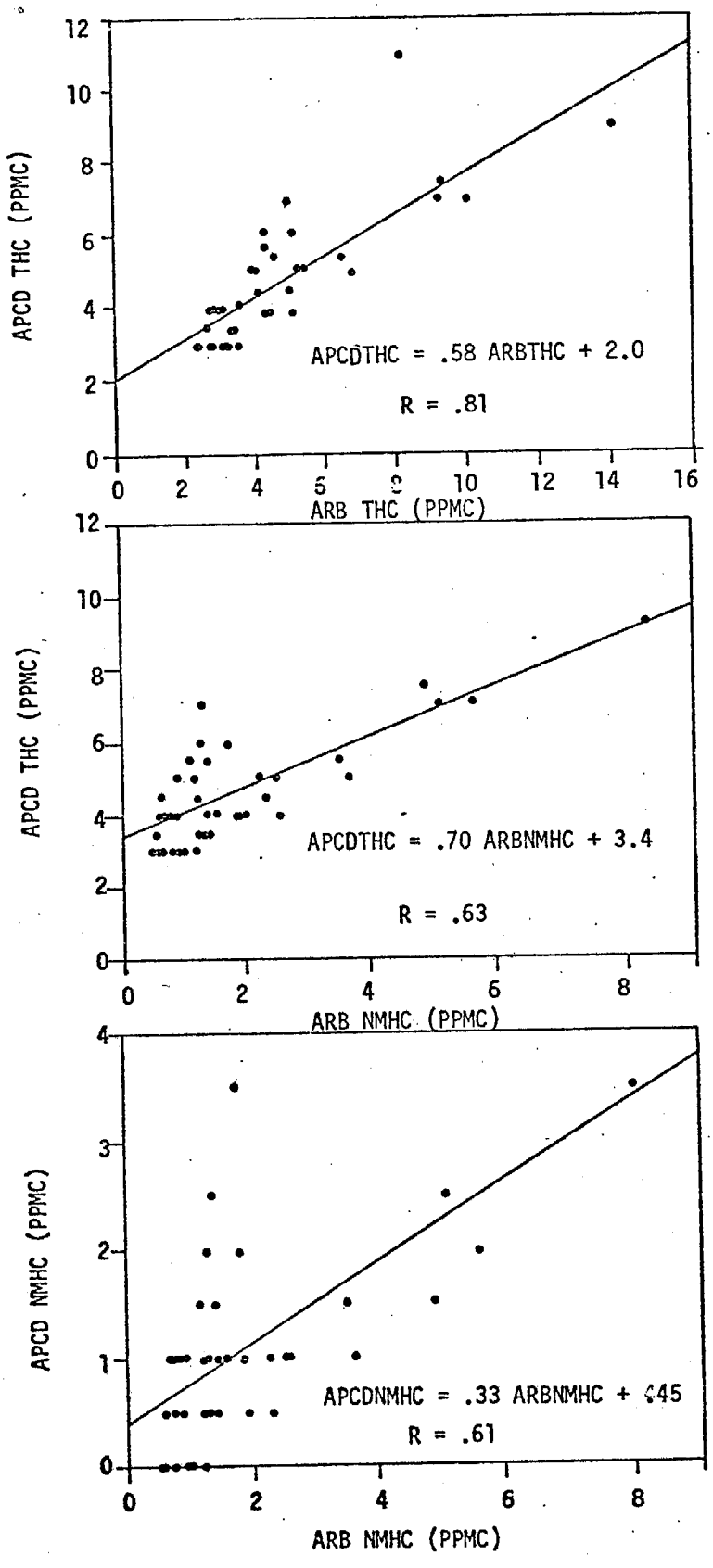


Figure 5.6 Comparison of APCD Hydrocarbon Data to ARB Field Test Data, Downtown Los Angeles, Aug. 2 - Oct. 14, 1971

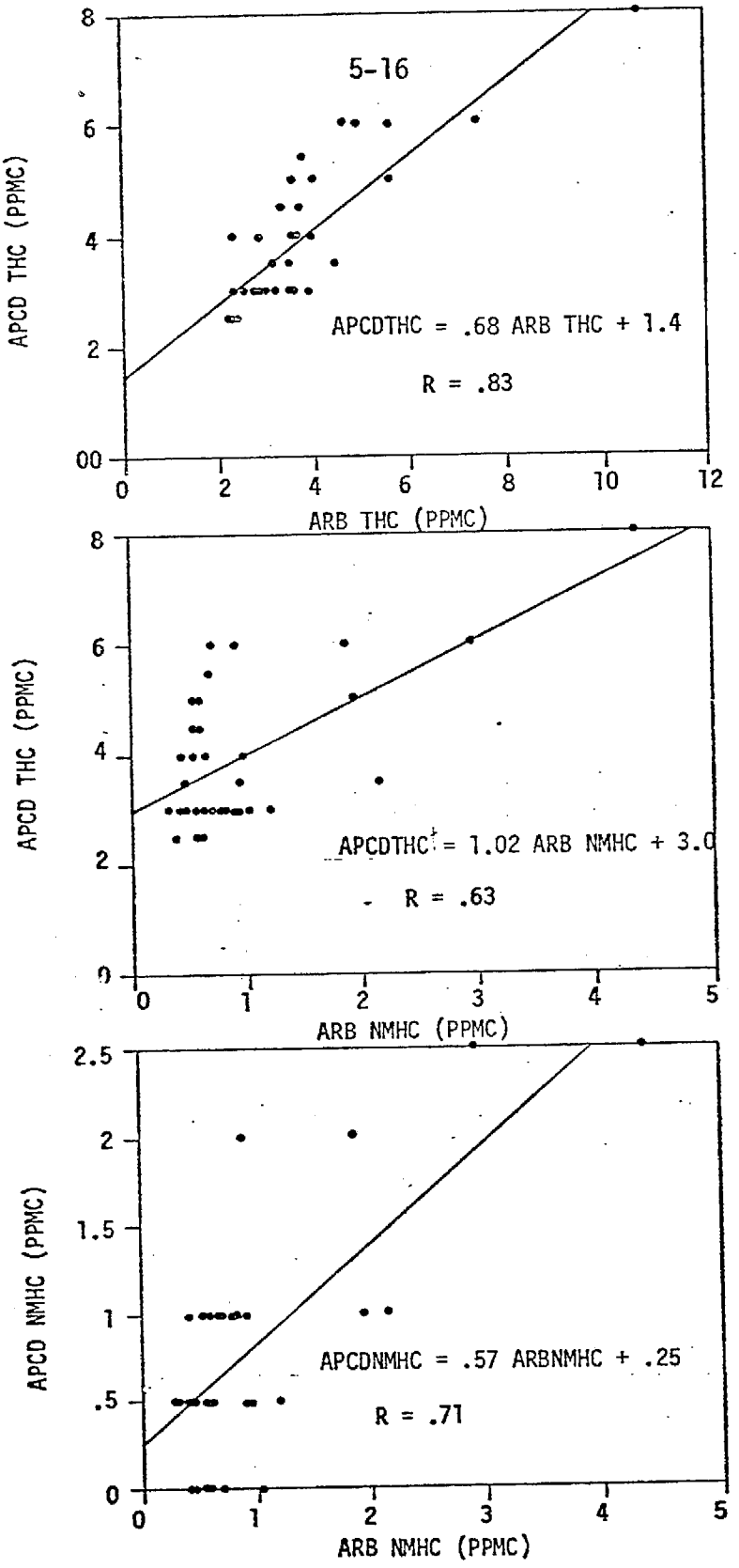


Figure 5.7. Comparison of APCD Hydrocarbon Data to ARB Field Test Data, Azusa, Aug. 2 - Oct. 14, 1971

Table 5.5 Correlation Coefficients of APCD Hydrocarbon Data with ARB Field Data, 1971

	APCD THC	APCD NMHC
Downtown Los Angeles		
ARB THC'	.81	--
ARB NMHC'	.63	.61
Azusa		
ARB THC'	.83	--
ARB NMHC'	.63	.71

Because THC and CH_4 are reported only to the nearest ppm, individual NMHC measurements can only assume values of 0, 1 ppm, 2 ppm, etc.* This is very poor resolution, considering that the 6:00-9:00 A.M. APCD NMHC measurements average less than 1 ppm. Because of the errors in the APCD NMHC data, the APCD THC data (adjusted to represent nonmethane hydrocarbons by a linear formula) appear to give as good or better indication of the fluctuations in nonmethane hydrocarbons than do the APCD NMHC data.

*Note the three-hour NMHC averages in Figures 5.4 and 5.5 can occur at 0, .33 ppm, .67 ppm, etc., while the two-hour averages in Figures 5.6 and 5.7 can occur at 0, .5 ppm, 1.0 ppm, etc.

5.3 REFERENCES

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3. Bonamassa, F., and H. Mayrsohn, "Distribution of Hydrocarbons in the Los Angeles Atmosphere, August-October 1971," California Air Resources Board, El Monte, 1971.

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5. Mayrsohn, H., M. Kuramoto, J. Crabtree, R. D. Sothern, and H. Mano, "A Trend Study of Two Indicator Hydrocarbons in the South Coast Air Basin," California Air Resources Board, June 1974.

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7. Mayrsohn, H., et al, "Atmospheric Hydrocarbon Concentrations," June-September 1974, California Air Resources Board, 1974.

8. Mayrsohn, H., et al, "Source Reconciliation of Atmospheric Hydrocarbons in the South Coast Air Basin, 1974, California Air Resources Board, July 1975.

9. Mayrsohn, H., et al, "Atmospheric Hydrocarbons Concentrations, June-September 1975," California Air Resources Board, January 1976.

10. Mayrsohn, Henry, El Monte Laboratories, Air Resources Board, Personal Communication, October 1976.

6.0 INTERSTATION CORRELATIONS

Since the empirical modeling analysis will be based on day-to-day fluctuations in oxidant and precusor concentrations, the data quality aspect of most concern is the precision with which daily pollution level variations are characterized. One way of assessing the quality of the data with respect to fluctuations is to examine the correlation of daily pollutant measurements between pairs of monitoring sites. It is difficult to attach meaning to the absolute magnitude of interstation correlation coefficients because daily fluctuations in pollutant levels will certainly not be uniform over the basin; in particular, low correlations might be expected for primary pollutants which are more sensitive to micro-scale meteorology than are secondary pollutants. However, by comparing correlation levels for different pollutants, one should be able to assess data quality for each pollutant relative to data quality for other pollutants.

The data for performing the interstation correlations were retrieved from Technology Service Corporation's bank of ARB and APCD data tapes. The pollutants examined included oxidant, NO_x, THC, and NMHC (the four contaminants of interest in the empirical modeling study) and, for comparison purposes, carbon monoxide. The correlations for the four primary contaminants were based on daily 6-9 AM averages, while the correlations for oxidant were based on daily maximum one hour concentrations. Separate correlations were run with data from 1969 and 1973 in order to determine whether data quality changed over time. All stations that could conceivably be used as source or receptor sites were included in the analysis.

Tables 6.1 through 6.5 present the interstation correlation coefficients for OX, NO_x, THC, NMHC, and CO, respectively. At the bottom of each table, the average correlation coefficient for each station against all other stations is listed. Also presented are the average correlation coefficients among all stations; these averages are further summarized in Table 6.6.

Table 6.6 Average Interstation Correlation Coefficients Among All Sites

POLLUTANT	INTERSTATION CORRELATIONS 1969	1973
OX	.67	.69
NO_x	.54	.57
THC	.45	.45
NMHC	.23	.37
CO	.44	.59

As indicated in Table 6.1, the highest interstation correlations occur in the case of oxidant. The average of all interstation correlations for oxidant was .67 in 1969 and .69 in 1973. Four stations in the central part of the basin (Azusa, Burbank, Pasadena, and Pomona) yield average correlations greater than .75 when paired against all other stations. In fact, the individual correlations among Azusa, Pasadena, and

Table 6.1 Interstation Correlation Coefficients for Daily Maximum One-Hour Oxidant Concentrations

1969 Data

	DOLA	Azusa	Burbank	Reseda	Pasadena	Pomona	Lennox	Whittier	Newhall	Anaheim	San Bern.	La Habra	Redlands
DOLA		.77	.84	.72	.84	.75	.65	.71	.38	.71	.67	.60	.57
Azusa	.77		.87	.83	.95	.93	.43	.81	.57	.82	.85	.82	.82
Burbank	.84	.87		.85	.92	.85	.50	.75	.50	.75	.81	.69	.68
Reseda	.72	.83	.85		.83	.84	.37	.60	.74	.65	.83	.55	.74
Pasadena (79)	.84	.95	.92	.83		.91	.49	.78	.51	.80	.85	.77	.80
Pomona	.75	.93	.85	.84	.91		.41	.69	.52	.80	.90	.73	.82
Lennox	.65	.43	.50	.37	.49	.41		.40	.14	.43	.33	.39	.25
Whittier	.71	.81	.75	.60	.78	.69	.40		.28	.88	.56	.86	.59
Newhall	.38	.57	.50	.74	.51	.52	.14	.28		.28	.52	.37	.50
Anaheim	.71	.82	.75	.65	.80	.80	.43	.88	.28		.73	.80	.66
San Bern.	.67	.85	.81	.83	.85	.90	.33	.56	.52	.73		.68	.82
La Habra	.60	.82	.69	.55	.77	.73	.39	.86	.37	.80	.68		.68
Redlands	.57	.82	.68	.74	.80	.82	.25	.59	.50	.66	.82	.68	
Average Against All Other Stations	.68	.70	.75	.71	.79	.76	.40	.66	.44	.69	.71	.66	.66

Average of All Interstation Correlations: .67

1973 Data

	DOLA	Azusa	Burbank	Reseda	Pasadena	Pomona	Lennox	Whittier	Newhall	Anaheim	San Bern.	La Habra	Palm Springs	Indio
DOLA		.79	.81	.70	.85	.76	.66	.71	.55	.73	.64	.75	.51	.50
Azusa	.79		.87	.85	.96	.94	.45	.69	.76	.77	.86	.82	.71	.69
Burbank	.81	.87		.86	.91	.87	.50	.71	.74	.70	.80	.76	.66	.65
Reseda	.70	.85	.86		.86	.86	.37	.56	.88	.61	.88	.65	.78	.76
Pasadena (83)	.85	.96	.91	.86		.91	.48	.71	.75	.76	.83	.80	.67	.68
Pomona	.76	.94	.87	.86	.91		.46	.71	.76	.76	.90	.83	.74	.72
Lennox	.66	.45	.50	.37	.48	.46		.64	.21	.59	.33	.59	.21	.20
Whittier	.71	.69	.71	.56	.71	.71	.64		.35	.81	.53	.88	.39	.37
Newhall	.55	.76	.74	.88	.75	.76	.21	.35		.46	.87	.47	.83	.81
Anaheim	.73	.77	.70	.61	.76	.76	.59	.81	.46		.65	.86	.54	.47
San Bern.	.64	.86	.80	.88	.83	.90	.33	.53	.87	.65		.66	.84	.81
La Habra	.75	.82	.76	.65	.80	.83	.59	.88	.47	.86	.66		.50	.45
Palm Springs	.51	.71	.66	.78	.67	.74	.21	.39	.83	.54	.84	.50		.86
Indio	.50	.69	.65	.76	.68	.72	.20	.37	.81	.47	.81	.45	.86	
Average Against All Other Stations	.69	.78	.76	.74	.78	.78	.44	.63	.65	.67	.74	.70	.63	.62

Average of All Interstation Correlations: .69

Table 6.2 Interstation Correlation Coefficients for 6-9 A.M. NO_x Concentrations

1969 Data

	DOLA	Azusa	Burbank	Reseda	Pasadena	Pomona	Lennox	Whittier	Anaheim	San Bern.	La Habra
DOLA		.36	.76	.51	.64	.62	.68	.69	.51	.42	.69
Azusa	.36		.47	.27	.52	.41	.01	.39	.30	.36	.55
Burbank	.76	.47		.77	.77	.74	.64	.72	.63	.38	.74
Reseda	.51	.27	.77		.60	.63	.51	.53	.47	.45	.56
Pasadena (79)	.64	.52	.77	.60		.77	.52	.62	.52	.41	.67
Pomona	.62	.41	.74	.63	.77		.61	.58	.54	.41	.64
Lennox	.68	.01	.64	.51	.52	.61		.58	.48	.22	.44
Whittier	.69	.39	.72	.53	.62	.58	.58		.72	.45	.82
Anaheim	.51	.30	.63	.47	.52	.54	.48	.72		.36	.76
San Bern.	.42	.36	.38	.45	.41	.41	.22	.45	.36		.33
La Habra	.69	.55	.74	.56	.67	.64	.44	.82	.76	.33	
Average Against All Other Stations	.59	.37	.66	.53	.60	.60	.47	.62	.53	.37	.62

Average of All Interstation Correlations: 0.54

1973 Data

	DOLA	Azusa	Burbank	Reseda	Pasadena	Pomona	Lennox	Whittier	Norwalk	Anaheim	San Bern.	La Habra
DOLA		.45	.69	.59	.70	.68	.74	.73	.55	.64	.43	.76
Azusa	.45		.45	.44	.39	.55	.19	.32	.36	.26	.40	.33
Burbank	.69	.45		.77	.70	.77	.72	.66	.67	.62	.43	.72
Reseda	.59	.44	.77		.60	.68	.61	.54	.71	.53	.46	.60
Pasadena (83)	.70	.39	.70	.60		.71	.67	.65	.61	.52	.48	.69
Pomona	.68	.55	.77	.68	.71		.62	.66	.63	.56	.51	.72
Lennox	.74	.19	.72	.61	.67	.62		.72	.59	.63	.35	.77
Whittier	.73	.32	.66	.54	.65	.66	.72		.51	.73	.29	.84
Newhall	.55	.36	.67	.71	.61	.63	.59	.51		.45	.56	.62
Anaheim	.64	.26	.62	.53	.52	.56	.63	.73	.45		.28	.69
San Bern.	.43	.40	.43	.46	.48	.51	.35	.29	.56	.28		.38
La Habra	.76	.33	.72	.60	.69	.72	.77	.84	.62	.69	.38	
Average Against All Other Stations	.63	.37	.65	.59	.61	.64	.61	.61	.57	.54	.42	.65

Average of All Interstation Correlations: 0.57

Table 6.3 Interstation Correlation Coefficients for 6-9 A.M. THC Concentrations

1969 Data

	DOLA	Azusa	Pasadena	Anaheim	San Bern.
DOLA		.58	.45	.64	.47
Azusa	.59		.57	.39	.44
Pasadena (79)	.45	.57		.26	.47
Anaheim	.64	.39	.26		.25
San Bern.	.47	.44	.47	.25	
Average Against All Other Stations	.54	.50	.44	.38	.41

Average of all Interstation Correlations: 0.45

1973 Data

	DOLA	Azusa	Burbank	Reseda	Pasadena	Pomona	Lennox	Whittier	Newhall	Anaheim	San Bern.
DOLA		.63	.62	.53	.57	.67	.58	.52	.24	.41	.44
Azusa	.63		.42	.40	.52	.64	.27	.27	.22	.24	.44
Burbank	.62	.42		.72	.52	.63	.67	.60	.21	.57	.48
Reseda	.53	.40	.72		.48	.62	.50	.52	.37	.48	.55
Pasadena (83)	.57	.52	.52	.48		.54	.41	.45	.30	.32	.46
Pomona	.67	.64	.63	.62	.54		.49	.49	.29	.45	.57
Lennox	.58	.27	.67	.50	.41	.49		.63	.12	.50	.30
Whittier	.52	.27	.60	.52	.45	.49	.63		.10	.67	.32
Newhall	.24	.22	.21	.37	.30	.29	.12	.10		.05	.45
Anaheim	.41	.24	.57	.48	.32	.45	.50	.67	.05		.24
San Bern.	.44	.44	.48	.55	.46	.57	.30	.32	.45	.24	
Average Against All Other Stations	.52	.40	.54	.52	.46	.54	.45	.46	.24	.39	.42

Average of All Interstation Correlations: 0.45

Table 6.4 Interstation Correlation Coefficients for 6-9 A.M. NMHC Concentrations

1969 Data

	DOLA	Azusa	Pasadena
DOLA		.36	.12
Azusa	.36		.22
Pasadena (79)	.12	.22	
Average Against All Other Stations	.24	.29	.17

Average of all Interstation Correlations: 0.23

1973 Data

	DOLA	Azusa	Burbank	Reseda	Pasadena	Pomona	Lennox	Whittier	Newhall
DOLA		.35	.50	.37	.37	.48	.49	.45	.25
Azusa	.35		.27	.25	.24	.32	.21	.20	.15
Burbank	.50	.27		.57	.55	.48	.54	.52	.33
Reseda	.37	.25	.57		.35	.39	.42	.40	.40
Pasadena (83)	.37	.24	.55	.35		.49	.40	.40	.18
Pomona	.48	.32	.48	.39	.49		.44	.46	.21
Lennox	.49	.21	.54	.42	.40	.44		.50	.25
Whittier	.45	.20	.52	.40	.40	.46	.50		.15
Newhall	.25	.15	.33	.40	.18	.21	.25	.15	
Average Against All Other Stations	.41	.25	.47	.39	.37	.41	.41	.38	.24

Average of All Interstation Correlations: 0.37

Table 6.5 Interstation Correlation Coefficients for 6-9 A.M. CO Concentrations

1969 Data

	DOLA	Azusa	Burbank	Reseda	Pasadena	Pomona	Lennox	Whittier	Anaheim	San Bern.	La Habra
DOLA		.51	.72	.60	.59	.69	.54	.64	.37	.37	.51
Azusa	.51		.30	.38	.51	.47	-.04	.02	.32	.46	.31
Burbank	.72	.30		.76	.65	.74	.66	.65	.25	.36	.59
Reseda	.60	.38	.76		.54	.68	.47	.53	.23	.41	.61
Pasadena (79)	.59	.51	.65	.54		.66	.43	.72	.11	.46	.45
Pomona	.69	.47	.74	.68	.66		.54	.54	.25	.45	.52
Lennox	.54	-.04	.66	.47	.43	.54		.58	.21	.12	.47
Whittier	.64	.02	.65	.53	.72	.54	.58		.34	.21	.00
Anaheim	.37	.32	.25	.23	.11	.25	.21	.34		.31	.22
San Bern.	.37	.46	.36	.41	.46	.45	.12	.21	.31		.27
La Habra	.51	.31	.59	.61	.45	.52	.47	.00	.22	.27	
Average Against All Other Stations	.55	.32	.57	.52	.51	.55	.40	.42	.26	.34	.40

Average of All Interstation Correlations: 0.44

1973 Data

	DOLA	Azusa	Burbank	Reseda	Pasadena	Pomona	Lennox	Whittier	Newhall	Anaheim	San Bern.	La Habra
DOLA		.58	.77	.64	.77	.68	.73	.70	.51	.67	.40	.67
Azusa	.58		.55	.47	.55	.71	.30	.37	.46	.48	.58	.33
Burbank	.77	.55		.83	.87	.69	.76	.73	.67	.66	.47	.69
Reseda	.64	.47	.83		.76	.58	.66	.60	.68	.60	.46	.62
Pasadena (83)	.77	.55	.87	.76		.72	.78	.75	.64	.63	.42	.75
Pomona	.68	.71	.69	.58	.72		.51	.54	.52	.57	.57	.55
Lennox	.73	.30	.76	.66	.78	.51		.79	.55	.57	.25	.76
Whittier	.70	.37	.73	.60	.75	.54	.79		.51	.67	.21	.78
Newhall	.51	.46	.67	.68	.64	.52	.55	.51		.47	.44	.53
Anaheim	.67	.48	.66	.60	.63	.57	.57	.67	.47		.37	.59
San Bern.	.40	.58	.47	.46	.42	.57	.25	.21	.44	.37		.26
La Habra	.67	.33	.69	.62	.75	.55	.76	.78	.53	.59	.26	
Average Against All Other Stations	.65	.49	.70	.63	.69	.60	.61	.60	.54	.57	.40	.59

Average of All Interstation Correlations: 0.59

Pomona range from .91 to .96! The only sites with relatively low average correlations are Lennox and Newhall, two special cases. Lennox is the only coastal site considered, while Newhall is north of the main valleys in the SCAB. Even the sites in the SEDAB (Palm Springs and Indio) yield good average correlations against the sites in the SCAB.

The high interstation correlations for oxidant occur for two reasons. The first reason is good data quality; the high quality of oxidant data has been discussed in both Chapter 4 and Chapter 5. The second reason is that oxidant is a secondary pollutant. Secondary pollutants tend to be more sensitive to regional scale meteorology (e.g., temperature, solar radiation, mixing height) than to the microscale meteorology at individual monitoring sites. The pervasive influence of regionwide meteorology leads to good oxidant correlations between some stations that are separated by 50 miles or more (see later, Figure 6.1).

Presumably due to the greater importance of microscale meteorology and local sources, the interstation correlations are lower for the primary pollutants (NO_x, THC, NMHC, and CO) than for oxidant. However, important conclusions concerning data quality can be reached by comparing relative correlation levels among the primary contaminants in Table 6.6. Among the primary pollutants, the highest quality data appears to be NO_x data (average R's of .54 and .57) and CO data in 1973 (average R of .59). The 1969 CO data (average R of .44) and the THC data (average R of .45 in both years) appear to be of somewhat lesser quality. Very low data quality is evident in the case of NMHC; the correlation coefficients for

NMHC are only .23 and .37 in the two years even though the NMHC data are restricted to locations in Los Angeles County only.

The relative quality of data for the primary pollutants can also be illustrated by examining subsets of the correlation tables. For instance, if we consider sites in Los Angeles County only, the average interstation correlations in 1973 are .64, .60, .47, and .37 for CO, NO_x, THC, and NMHC, respectively. If we consider the central Los Angeles County stations (Downtown LA, Burbank, and Pasadena), the average intercorrelations in 1973 are .80, .70, .57, and .47 for CO, NO_x, THC, and NMHC, respectively.

The credibility of the comparisons among the various primary pollutants is enhanced by the consistent patterns found in Tables 6.2 to 6.5. For instance, the average interstation correlations for primary pollutants are almost always highest at the Burbank station. Low average interstation correlations consistently occur for Azusa, Lennox, San Bernardino, Newhall, and Anaheim.

An interesting way of examining the correlation data is to plot the correlations against interstation distance. Figures 6.1 through 6.5 present such plots for OX, NO_x, THC, NMHC, and CO, respectively. These figures indicate that correlations tend to increase as the distances between stations become smaller. Figure 6.1 illustrates the particularly high correlations for oxidant. Figures 6.2 to 6.5 show, in graphical fashion, that the CO and NO_x data are of higher quality than THC data, which in turn are of higher quality than NMHC data.

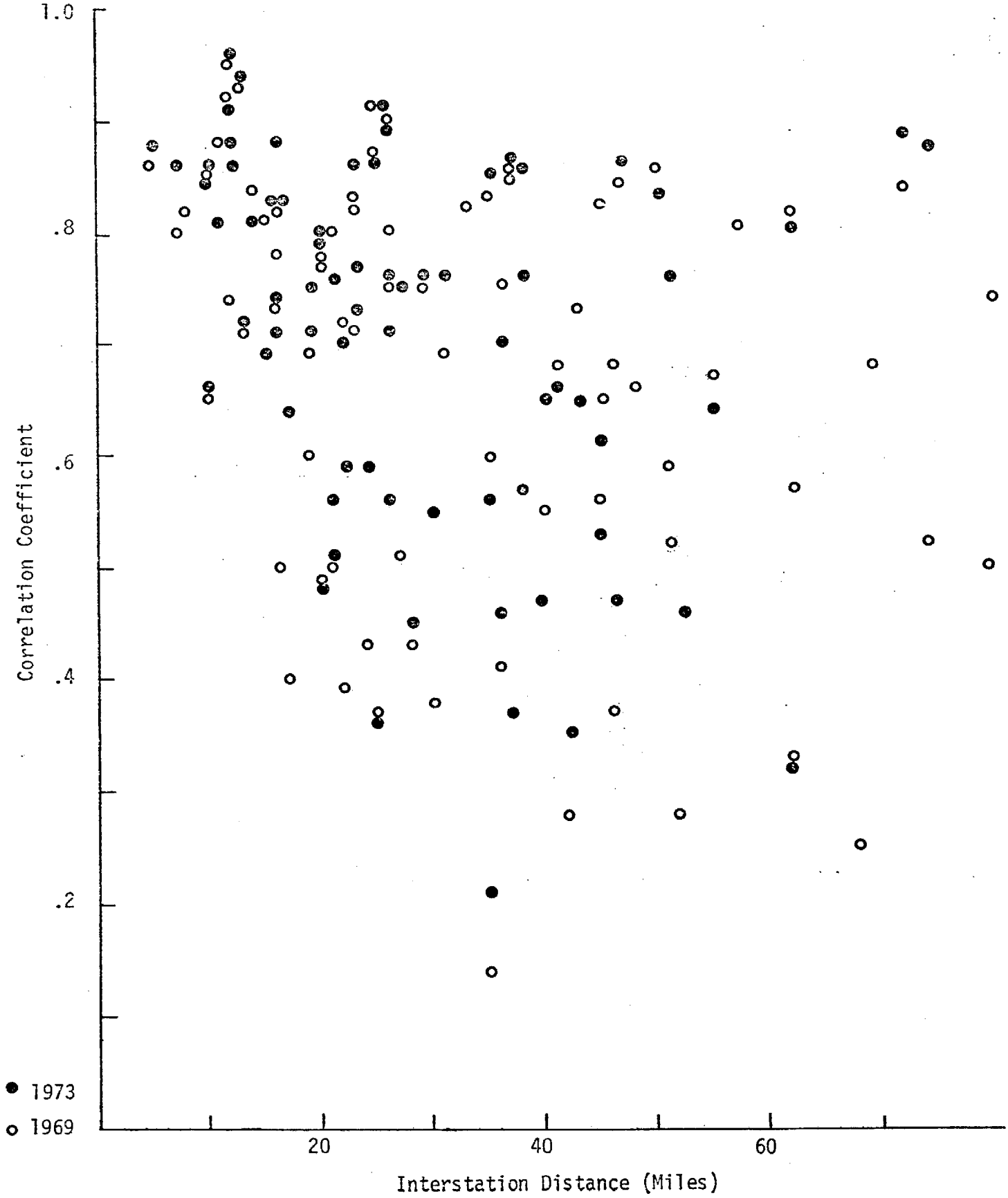

Figure 6.1 Daily Maximum Oxidant Correlations vs. Interstation Distance

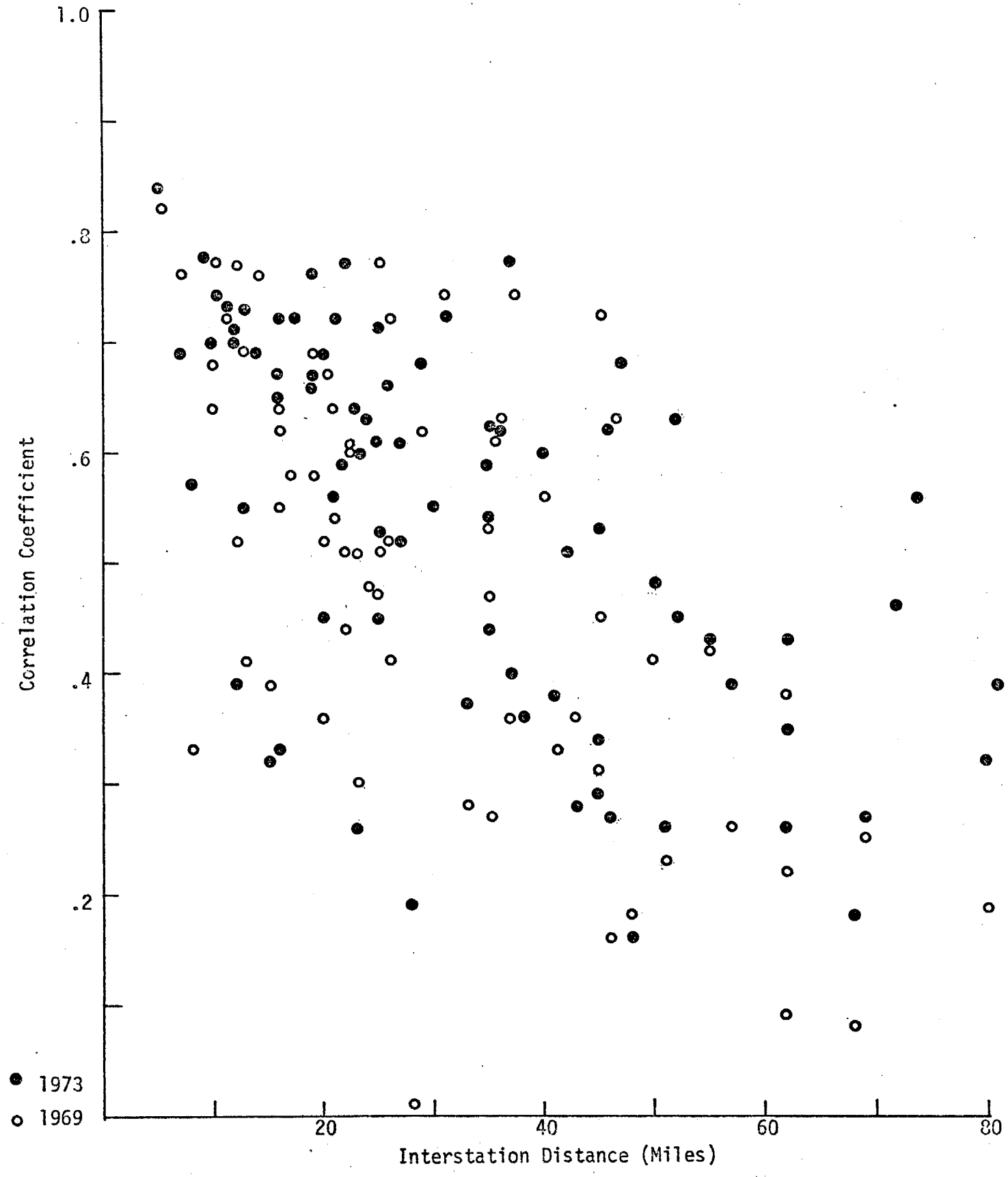

Figure 6.2 6-9 A.M. NO_x Correlations vs. Interstation Distance

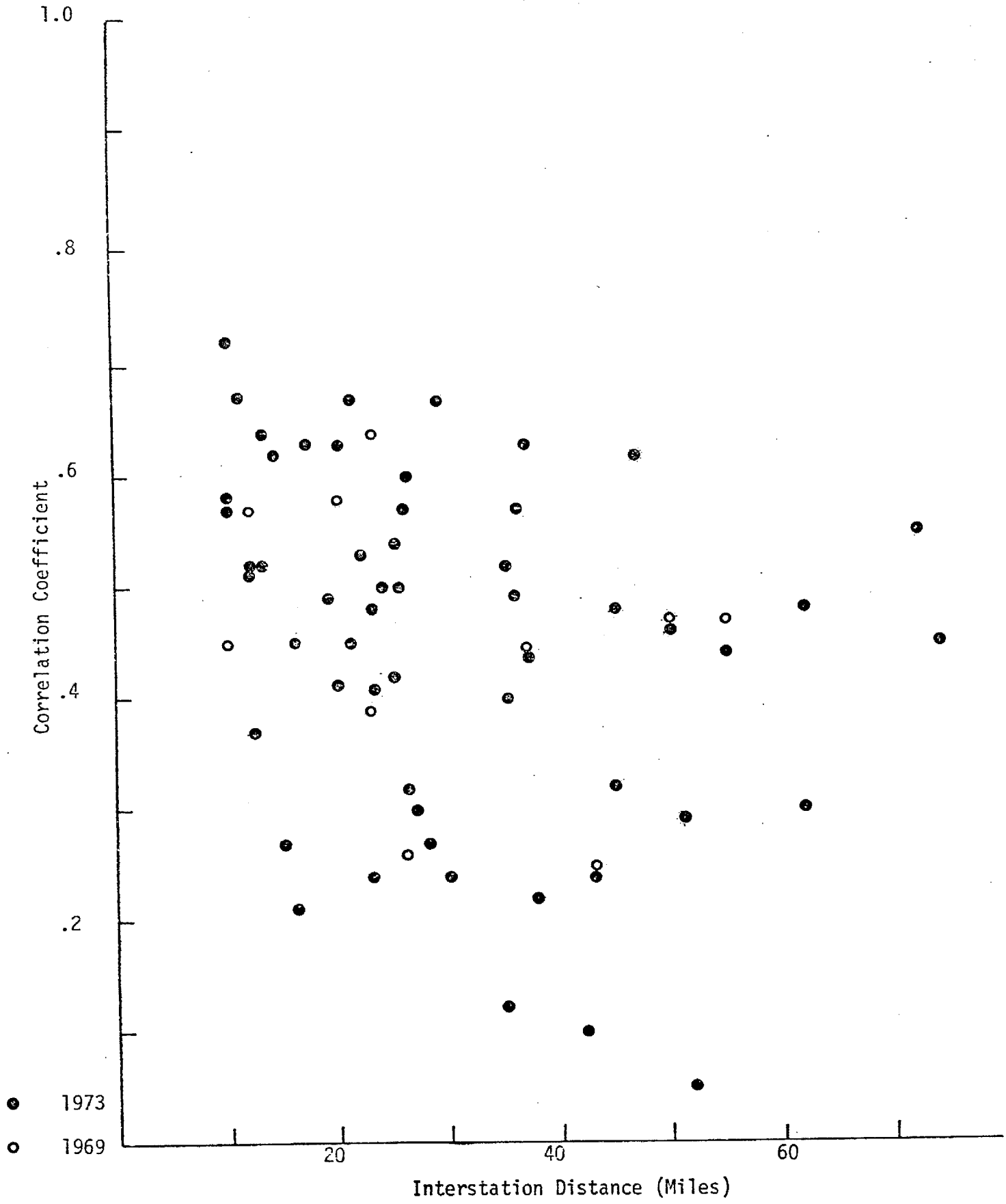

Figure 6.3 6-9 A.M. THC Correlations vs. Interstation Distance

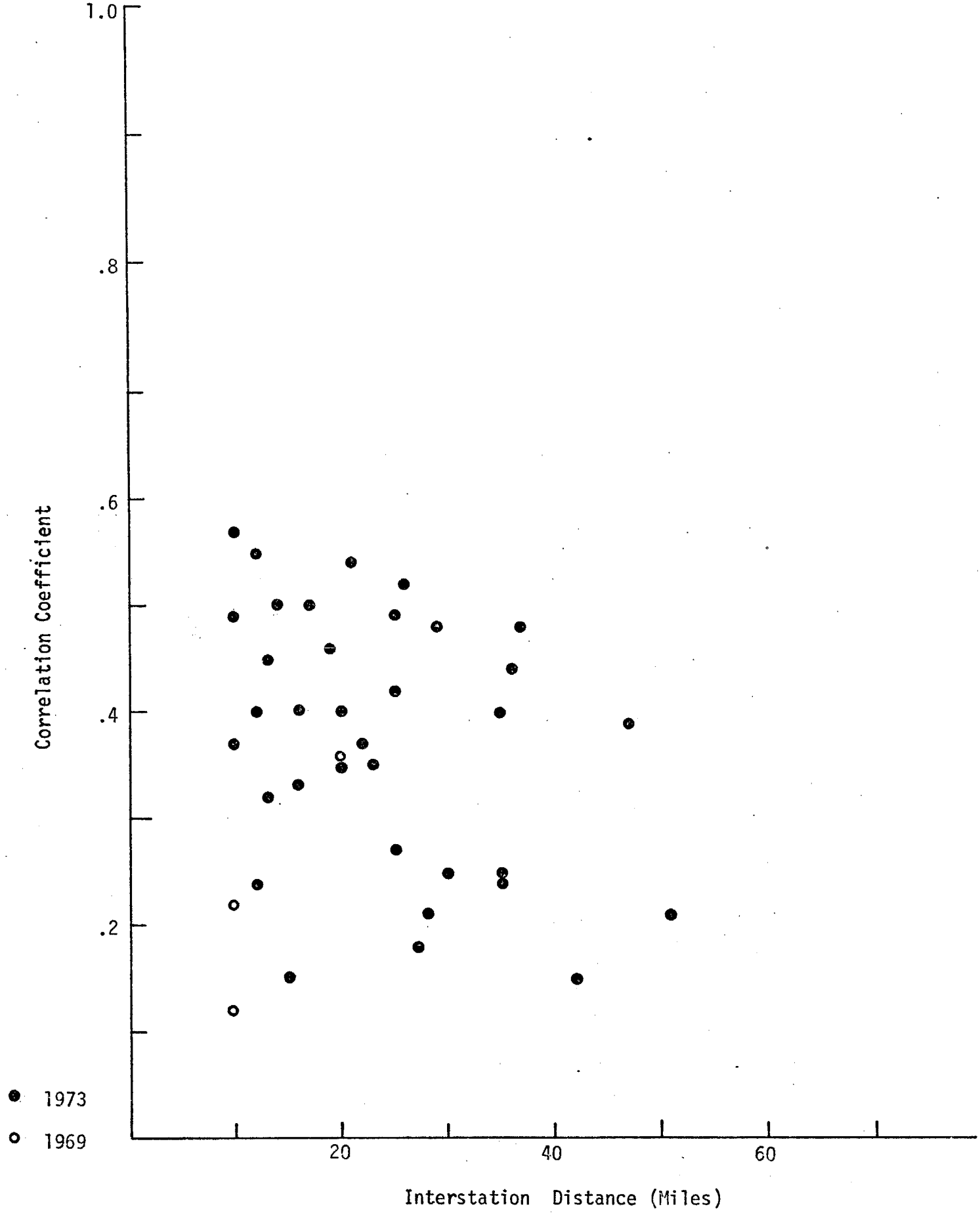

Figure 6.4 6-9 A.M. NMHC Correlations vs. Interstation Distance

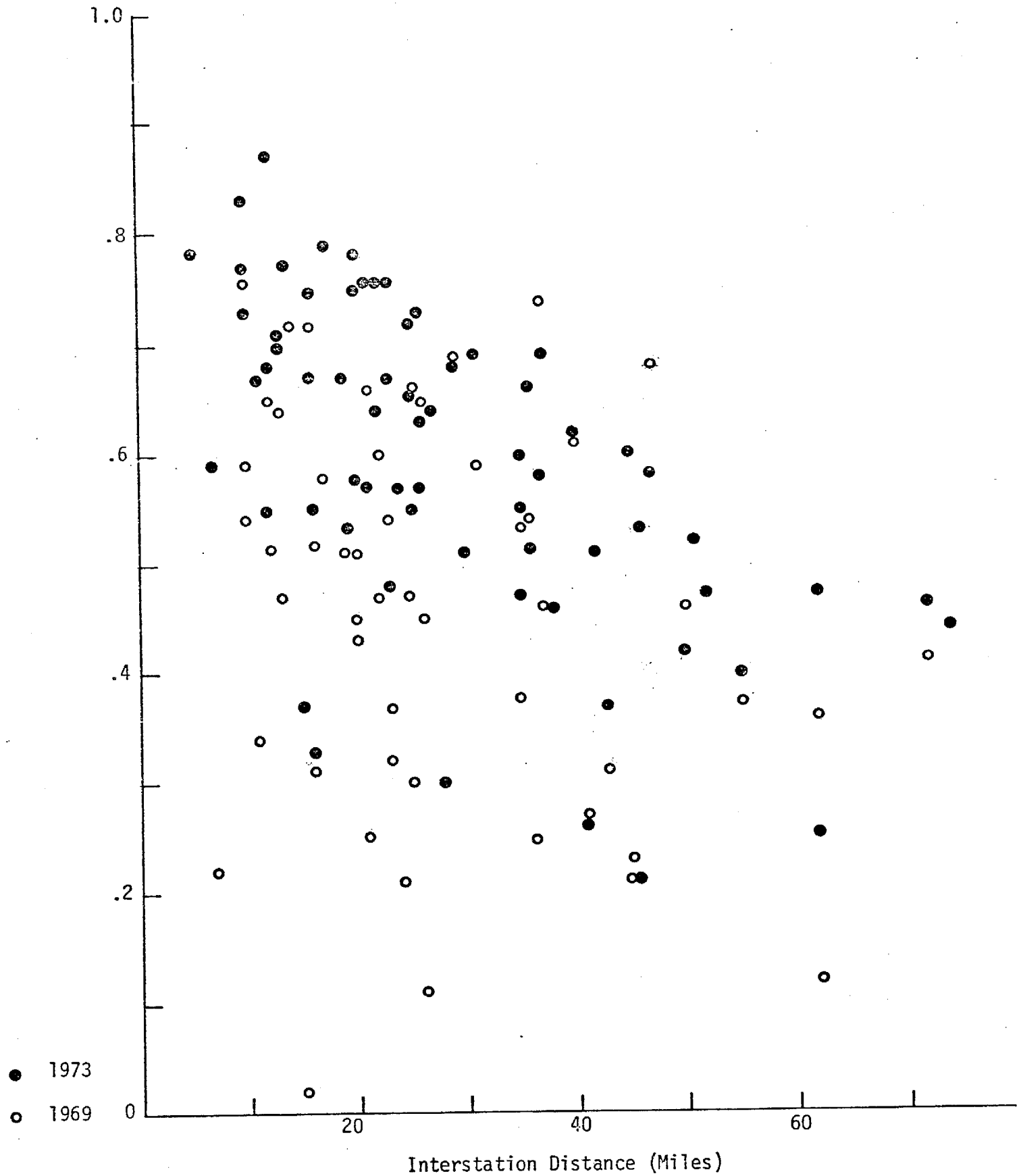

Figure 6.5 6-9 A.M. CO Correlations vs. Interstation Distance

This chapter demonstrates further the inadvisability of using NMHC data in the empirical modeling study. Although low interstation correlations do not prove that a given set of data is bad, they do cast doubts concerning the validity and consistency of that data set. Since the THC data have significantly higher interstation correlations than do the NMHC values, the former are more appropriate for empirical modeling, even though the latter would be preferable on physical grounds.

7.0 FINDINGS AND CONCLUSIONS

The purpose of this interim report is to survey the availability of aerometric data in the SCAB and SEDAB, to identify potential source and receptor sites, and to assess the quality of the data base. In essence, the objective is to investigate whether or not the existing data base is sufficiently comprehensive and accurate for empirical modeling of the oxidant/precursor relationship. The findings and conclusions that have resulted from this investigation are summarized in the paragraphs which follow.

There is little question that enough aerometric data are available to permit a detailed empirical modeling study (Chapter 2). There are sixteen oxidant monitoring sites in the SCAB, five oxidant monitoring sites in the SEDAB, and twelve precursor (THC and NO_x) monitoring sites in the SCAB that satisfy a criterion of at least three years of 75% complete data. There are also numerous sites providing wind field data and temperature measurements. Data on mixing heights, solar radiation, and relative humidity are limited but are still comprehensive enough to be used in the modeling analysis. All of the necessary air quality data and much of the meteorological data are available in computerized form.

A westerly sea breeze flow is the most prevalent wind pattern during daylight hours in the June-October photochemical smog season (Chapter 3). This wind pattern often involves a southerly component during the morning hours. The daytime sea breeze flow is so frequent in the photochemical smog season that restricting the empirical modeling analysis to days with this pattern will not significantly reduce the number of days in the data base.

For the dominant westerly flow pattern, it is possible to identify at least five groups of source/receptor monitoring sites representing varying degrees of transport distance and varying degrees of reaction time (Chapter 3). At one extreme is local late-morning oxidant in Downtown Los Angeles, while at the other extreme is transported evening oxidant in Banning and Palm Springs. In the initial empirical modeling work, specific monitoring sites within the source and receptor areas should be selected based on an analysis of daily wind patterns and on preliminary correlations between precursor measurements and oxidant measurements. This preliminary statistical analysis will allow a more finely tuned assessment of the transport relationships between source sites and receptor sites.

A critical review of monitoring methods (Chapter 4) and statistical tests of data quality (Chapters 5 and 6) lead to consistent conclusions concerning the quality of oxidant and precursor measurements. Since the empirical modeling analysis will be based on day-to-day fluctuations in pollutant concentrations, the data quality aspect of most interest is the precision with which fluctuations in pollutant levels are measured. In general terms, the precision of the data for the pollutants of interest can be summarized as follows:

OX/O_3 - - - - - - - - Excellent

NO_x - - - - - - - - Good

THC - - - - - - - - Fair

NMHC - - - - - - - - Poor

For comparison purposes, the precision for two other pollutants examined in Chapter 5 is

NO_2 - - - - - - - - - Good

CO - - - - - - - - - Good

Nearly all of the routine oxidant/ozone data in the SCAB and SEDAB consists of KI oxidant measurements. In order to make all the KI data consistent, measurements taken by agencies other than the Los Angeles County APCD should be multiplied by a factor of 0.8 to account for calibration differences. To improve the accuracy of the KI data in representing ozone, interference corrections should be made according to

$$[O_3] = [OX] + [SO_2] - .2[NO_2] \quad .$$

Routine NMHC data, available for Los Angeles County only, exhibit poor quality for three reasons: 1) the methane separation methods tend to be error-prone and sensitive to operator technique, 2) errors are compounded by subtracting one uncertain measurement (CH_4) from another uncertain measurement (THC), and 3) large round-off errors occur because pre-1975 data are reported only to the nearest ppm. Low data quality precludes the use of NMHC measurements in the empirical modeling analysis.

It may be feasible to conduct a meaningful empirical modeling study using data for oxidant/ozone, NO_x, and THC. The main impediment to this would be the "fair" quality of the THC data and the approximations made in estimating NMHC concentrations from THC data. Some encouragement can be gained from previous empirical studies which have used THC data in the SCAB and which have obtained reasonable results in light of the limitations in the empirical models which were tried.[1,2,3,4] If the proposed modeling study is performed,

the preliminary statistical analysis of oxidant/precursor correlations (discussed earlier) should be used to help select precursor sites with the best quality THC data.*

*That THC data quality can vary from site to site is evidenced by the results of Chapters 4, 5, and 6.

7.1 REFERENCES

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3. Trijonis, J., "Economic Air Pollution Control Model for Los Angeles County in 1975," Environmental Science and Technology, Vol. 8, No. 9, September 1974.

4. Schuck, E., and R. Papetti, "Examination of the Photochemical Air Pollution Problem in the Southern California Area," EPA Internal Working Paper, May 1973.